Study on CO_2 Corrosion in Oil Producing Well

by

Mohd Noor Hazman bin Mansor

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
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(MECHANICAL ENGINEERING)

Approved by,

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Assoc. Prof. Dr. Razali Hamzah

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TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD NOOR HAZMAN BIN MANSOR

ABSTRACT

The purpose of this project is to study the CO_2 corrosion in oil production wells and the focus of the study will be on the tubing component of the production string. The main objectives of the project are; a) To study the material used in a well production string. b) To determine the average CO_2 corrosion rate of a typical well production string. As for the problem statement of this project, in oil and gas industry, CO_2 corrosion has been a recognized problem in production and transportation facilities for many years e.g. in the tubing string of an oil producing well. The corroded tubing will cause leakage and tubing failure hence, disrupt oil production. The scopes of study for this project consist of identifying the rate of CO2 corrosion during the production life time of the tubing string and determine the factors leading to the CO_2 corrosion. In order to provide a reliable prediction on the behavior of CO_2 corrosion on tubing steel, the project's methodology used Weight Loss Method using Autoclave Machine and Linear Polarization Resistance Method (LPR) to simulate the actual environment in the tubing during the oil production and analyze the CO_2 corrosion rate. The laboratory experiments are conducted on API L 80 type steel. The Weighted Loss Method is conducted in stagnant condition using 3 wt% NaCl over a series of parameters which includes pressure = 10 bar, 40 bar and 60 bar, pH=5 and temperature at 25℃. The LPR method is conducted in flowing solution using 3 wt% NaCl over a series of parameters which includes temperature = 25 ˚C, 40 ˚C and 60 ˚C, pH = 5 and pressure at 1 atm. All data were collected and analyzed using Weighted Loss Method, LPR, SEM, OM and Hardness (Vicker) Test to determine the CO_2 corrosion rate and the effects on the L 80 steel. As for the findings, the average CO_2 corrosion rates in API L 80 steel yield from the laboratory test ranges from 1.3 mm/yr to 4.7 mm/yr.

Keywords

CO_2 corrosion rate, $FeCO_3$ film layers, Weighted Loss Method, LPR Method, API L-80 steel, SEM, Vicker Test

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Corrosion is the degradation of the material due to chemical reaction with the environment. Corrosion problem is becoming an increasing threat to the integrity of oil field structures including pipelines, casing and tubing [1]. It is a serious problem in oil and gas industry all over the world. Most of the oil field structures encountered the corrosion problem because most of the equipments are made from steel and the natural existence of corroding agents to initiate the chemical reaction. Although high cost corrosion resistance alloys (CRAs) were developed to be able to resist the corrosion, steel is still the most cost effective material used in oil and gas facilities and structures [3]. The concern on the high cost remedial process for corrosion problematic well leads to the initiation of this project.

The tubing string is the most frequent component in a production well that will be corroded. The presence of CO_2 in produced fluids can result in very high corrosion rate particularly where the mode of attack on the tubing steel is localized. An aqueous phase is normally associated with the oil and gas being produced by the well [1]. The inherent corrosivity of this aqueous phase is dependent on the concentration of dissolved acidic gases and the water chemistry. The presences of CO_2 with the combination of water make the production potentially very corrosive.

CO_2 corrosion rate is dependent on the environmental effects such as temperature, pressure, pH, CO_2 partial pressure, flow velocity, CO_2 concentration and the formation of $FeCO_3$ layers [8]. The analysis of CO_2 corrosion rates have been carried out extensively to provide a reliable prediction on the behavior of CO_2 corrosion and leads to cost-effective and safe design of facilities used in the oil and gas industry.

In order to predict the behavior of CO_2 corrosion, Weight Loss Method and Linear Polarization Resistance Method (LPR) will be used to analyze both CO_2 corrosion rate and the effects on the tubing steel.

1.2 Problem Statement

Study on CO_2 corrosion has been carried out extensively for many years to observe the behavior of CO_2 corrosion on the steel in production facilities used in the oil and gas industry. The main reason in conducting the study and analysis is to gain understanding on CO_2 corrosion rate in the tubing component of oil producing string.

1.2.1 Problem Identification

Most of the studies on CO_2 corrosion rate were focused in the pipeline and platform materials such as API X-52, X-56, X-60, X-65 and N-80 steel. The study on CO_2 corrosion in the production tubing steel, API L-80 steel is crucial as the production fluid from the reservoir contains numerous amount of CO_2 gas which is typically 5% to 10% v/v in Malaysia's oilfields. Most of the oil producing wells in Malaysia are gas lifted wells and produced high in gas-oil-ratio (GOR). However, the concentration of CO_2 gas is different in different oil producing well. In gas lifted well, CO_2 gas is pumped into the production well to enhance the oil production and caused high concentration of CO_2 gas in the well.

1.2.2 Significance of the Project

The aim of this project was to study and analyze CO_2 corrosion effects and CO_2 corrosion rate using Weight Loss Method and LPR Method. It is important to understand the behavior of CO_2 corrosion in API L-80 steel and the ranges of CO_2 corrosion rate to minimize the CO_2 corrosion failure in oil producing string and lead to cost-effective and safe design of production facilities used in the oil and gas industry.

1.3 Objectives

The objectives of this project were:

a. To study the material used in the well production string
b. To determine the average CO_2 corrosion rate of a typical well production string

1.4 Scope of Study

The scopes of study of this project were:

a. To conduct the CO_2 corrosion test on API L-80 steel using Weight Loss Method and Linear Polarization Resistance Method.
b. To study and analyze the effect CO_2 corrosion on API L-80 steel using Scanning Electronic Microscopy (SEM) and Optical Microscope (OM) test.

1.5 Relevancy of the Project

The study of CO_2 corrosion in oil producing well is important especially in oil and gas industry. The results obtained from the laboratory tests will help to provide better understanding on the behavior of CO_2 corrosion. A thorough understanding on the effects of CO_2 corrosion and CO_2 corrosion rate in API L-80 will provide useful information thus help in providing reliable prediction of CO_2 corrosion which leads to cost-effective and safe design of production tubing used in the oil producing well.

1.6 Feasibility of the Project

The project was started by collecting reading materials such as books, journals and technical papers specifically on oil producing string components, CO_2 corrosion of steel, Weight Loss Method using Autoclave manual and LPR technique. Research was done continuously throughout this project to get a better understanding. The project was then focused on conducting laboratory experiments on API L-80 steel in CO_2 environment whereby analysis were carried out using Weight Loss Method, LPR and other techniques such as SEM, OM and Hardness (Vicker) Testing to determine the CO_2 corrosion rate and effects.

CHAPTER 2
LITERATURE REVIEW

In order to gain better understanding in the CO_2 corrosion phenomena that may occurred in oil producing string, study on the basic types of oil producing wells and well completion was a necessity.

2.1 Types of Oil Producing Well

Development or producing well is a hole drilled through the Earth's surface designed to find or produce petroleum oil hydrocarbon from the reservoir. The life cycle of an oil production string may lasts up to more than 50 years and corrosion is one of the factors that shorten the life cycle of the facilities [5].

Study on the CO_2 corrosion in oil producing string is crucial since numerous amount of carbon dioxide (CO_2) gas is produced along with the oil. There are 3 types of oil producing well. The details of these wells are as shown below.

2.1.1 Vertical Well

The most common oil producing wells are drilled vertically (refer to Figure 1.1). This is generally the least expensive option to penetrate a single target. If the surface location is not fixed then the rig can be placed above the desired target to allow a vertical penetration to the desired reservoir location. A vertical well can also be drilled through several stacked reservoirs to produce through the vertical wellbore [3].

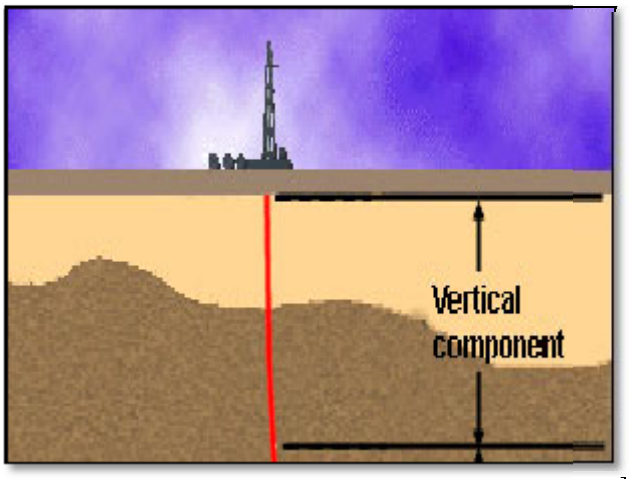


Figure 2.1: Directional/ Vertical Well

2.1.2 Deviated Well

A normal deviated well (single bore, less than 60° inclination) is the most common type of well currently drilled (refer to Figure 1.2). Many development wells are drilled as a group of wells from a single surface location and this requires directional wells for optimum spacing in the reservoir [3].

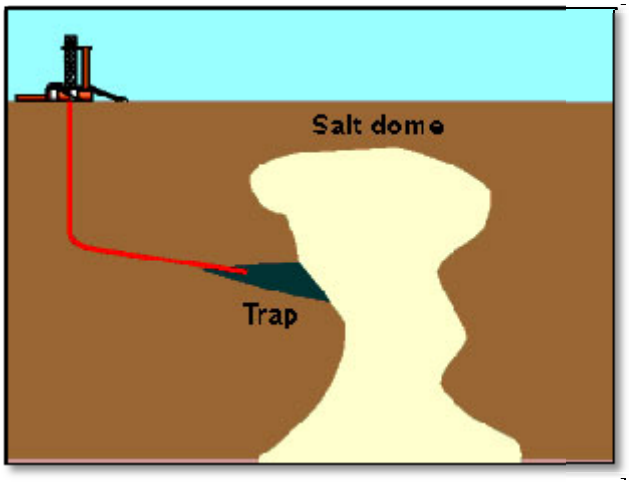


Figure 2.2: Deviated Well

2.1.3 Horizontal and Multilateral Well

Horizontal and multilateral wells (refer to Figure 1.3) have gained enormously in popularity. This type of well provide a lot of advantages compared to the

other types since it improves the surface of area contact between the wellbore and the formation [6]. Thus, it will enhance the production to the optimum.

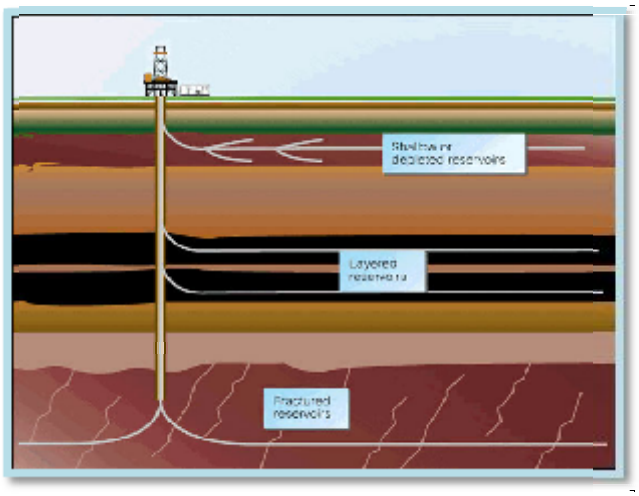


Figure 2.3: Horizontal and Multilateral Well

2.2 Components of a Typical Oil Producing Well

The typical type of oil producing well completion is the Cased, Cemented and Perforated Completion (refer to Figure 1.4) [3]. This type of completion is the most common because of its ability to effectively isolate the producing zone and by-pass the damaged portion of the bore hole. Either casing or liner is run across the reservoir and cemented into place, providing excellent hole protection.

Production tubing is run in the casing as close as possible to the reservoir and the reservoir section isolated using packers. The casing/liner across the reservoir section is then perforated (by-passing the filter cake and damaged zone), allowing production of the hydrocarbons [6]. Typical well completion consists of:

a. Wellhead
b. Casing
c. Tubing
d. Production Packer

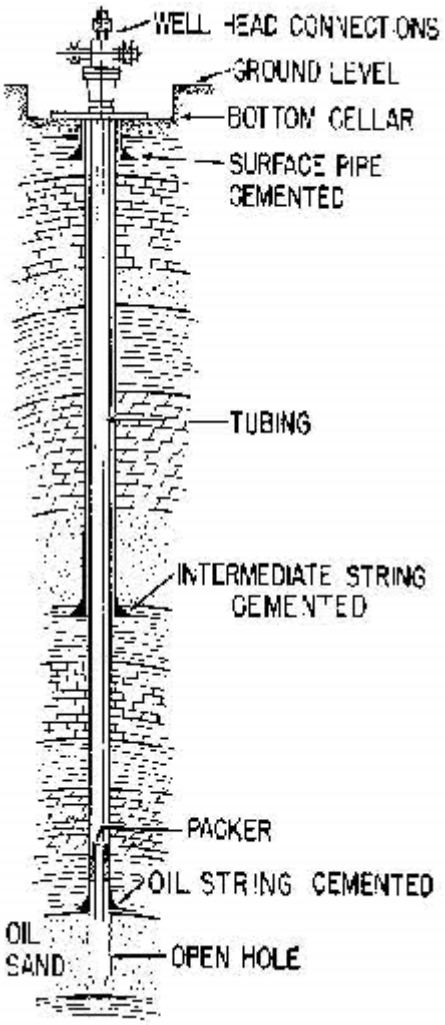


Figure 2.4: Cased, Cemented and Perforated Completion

2.2.1 Wellhead

Wellhead or Christmas Tree is the equipment installed at the surface of the wellbore to suspend the casings string. It consist of casing and tubing head, casing and tubing hangers, packoff and isolation seals, blow-out preventors and several valves. The functions of a wellhead are to suspend the string, casing pressure isolation and provide well access.

Wellhead components are mainly made of carbon steel and stainless steel [5]. Most of the external corrosion problem at wellhead is due to the existence of oxygen (O_2) at the surface. CO_2 corrosion mainly occurred on the internal surface of the wellhead.

2.2.2 Casing

Casing is a steel pipe which is run into the hole and cemented in place. Casing is used to protect a section of drilled hole and to provide a pressure vessel for drilling deeper and/or containing the production tubing strings through which hydrocarbons flow as the well is produced. Table 1.1 below shows different types of casing string.

Table 2.1: Casing Intervals

Types	Size (inch)
Conductor casing	30
Surface casing	28
Intermediate casing (optional)	13
Production casing	9

The conductor casing serves as a support during drilling operations, to flowback returns during drilling and cementing of the surface casing, and to prevent collapse of the loose soil near the surface. The surface casing is to isolate freshwater zones so that they are not contaminated during drilling and completion. The intermediate casing may be necessary on longer drilling intervals where necessary drilling mud weight to prevent blowouts may cause a hydrostatic pressure that can fracture deeper formations. The production casing string extends to the surface where it is hung off.

Few wells actually produce through casing, since producing fluids can corrode steel or form deposits such as asphaltenes or paraffins and the larger diameter can make flow unstable [6].

Most of the casing string is made of API J-55, K-55, N-80 or H-40 steel. The material may corrode over time and potentially expose to CO_2 corrosion since the string is on the sub surface. However, the casing string is sealed and isolated from any contact to the environment by cementing process. CO_2 corrosion may occur in the casing string if the cementing process is not done properly and caused communications between the casing and the seawater.

2.2.3 Production Packer

A production packer is a standard component of the completion hardware of oil or gas production wells used to provide a seal between the outside of the production tubing and the inside of the casing, liner, or wellbore wall [6]. Based on its primary use, packers can be divided into two main categories:

a. Production packers
b. Service packers.

Production packers are those that remain in the well during well production. Service packers are used temporarily during well service activities such as cement squeezing, acidizing, fracturing and well testing.

Material used in construction of production packer is stainless steel with 9% or higher chromium which is highly resistance to the CO_2 corrosion. Most of the corrosion problem encountered in the production packers is due to bimetallic or galvanic corrosion since the packers are in contact with different material used in casing or tubing string [1].

2.2.4 Tubing

Production tubing is a tubular used in a wellbore through which production fluids are produced. Production tubing provides a continuous bore from the production zone to the wellhead. It is usually between five and ten centimeters in diameter and is held inside the casing through the use of expandable packing devices. If there is more than one zone of production in the well, up to four lines of production tubing can be run [3].

Production tubing is used without cement in the smallest casing of a well completion to contain production fluids and convey them to the surface from an underground reservoir. The production tubing has a direct contact to the production fluids where CO_2 and water may be produced along with oil and CO_2 corrosion is a main threat to the tubing steel.

The production tubing material is made of API L-80 steel. The chemical composition of the steel is shown in Table 1.2 below. Figure 1.5 below shows the API L-80 steel that the student acquired from PETRONAS Carigali Sdn. Bhd. (PMO).

Table 2.2: Chemical composition of API L-80 steel

Element	Composition (%)
Carbon	0.15-0.21
Silicon	0.16-1.0
Manganese	0.35-1.0
Chromium	10.4-14.0
Phosporus	max 0.020
Sulphur	max 0.0050
Aluminium	0.025-0.050
Ferum	remainder

The minimum yield strength = 80 000 psi

The maximum yield strength = 95 000 psi

The minimum tensile strength = 95 000 psi

The hardness = 23 HRC

Figure 2.5: API L-80 steel

Most of the oil producing well in Malaysia is gas-lifted well or high gas oil ratio (GOR) well. In the gas-lifted well, the CO_2 corrosion is more likely to occur at the connection of gas lift valves and the tubing surface. The natural gas that used

to enhance the oil production contains numerous amount of carbon dioxide (CO_2) gas. As for the high GOR wells, carbon dioxide (CO_2) gas is highly soluble in the producing fluids where water and other gases is produced along the oil. The detail about the particles flow in the producing fluids is discussed in Section 2.3. When the CO_2 reacts with water, it becomes the ideal condition for CO_2 corrosion to occur. The details on the chemical reaction that leads to CO_2 corrosion is discussed in Section 2.4.

2.3 Particles Flow in the Oil Producing Well

Fluids and solid particles in the formations that flow up to the surface through the production tubing is the main contributor to the CO_2 corrosion problem in oil producing wells. Most of the wells produced raw liquid that is consists of oil, water, gas and some other solid particles such as sand.

2.3.1 Hydrocarbon

Hydrocarbon or petroleum oil originates from a small fraction of the organic matter deposited in sedimentary basins. Most of the organic matter is the remains of plants and animals that lived in the sea, and the rest is land-delivered organic matter carried in by rivers and continental runoff, or by winds [5]. These immediately condense into nitrogenous and humus complexes progenitors of kerogen. Some hydrocarbons are deposited in the sediments, but most form from thermal alteration at depth.

2.3.2 Gases

There are five (5) types of natural gas that is usually found in the production fluids [1]:

a. Methane, CH_4
b. Hydrogen Sulfide, H_2S
c. Carbon Dioxide, CO_2
d. Nitrogen, N_2
e. Helium, He

Methane is formed by bacterial decay of organic material. It is a major product of the diagenesis of coal and is given off from all forms of organic matter during diagenesis [6]. Hydrogen sulfide originates from the reduction of sulfates in the sediments and from sulfur compounds in petroleum and kerogen. Carbon dioxide is derived from the decarboxylation of organic matter, and from HCO_3 and $CaCO_3$. Nitrogen is derived from the nitrogen in organic matter and from trapped air. Helium is derived from the radioactive decay of uranium and thorium.

During the oil genesis and coalification process, the order of generation is generally carbon dioxide, nitrogen and methane. In most of the natural gases, the greatest individual component is methane typically 85 to 95% v/v. Levels of carbon dioxide (CO_2) are nominally 5% to 10% v/v. The combination of carbon dioxide (CO_2) gas and water is highly corrosive.

2.3.3 Produced Water

Produced water is water trapped in underground formations that is brought to the surface along with oil or gas. It is by far the largest volume by-product or waste stream associated with oil and gas production. On average, about 7 to 10 bbl produced water generated per 1 bbl of oil [5]. The formation structure indicates that most of the geological structure of the formation contains water which is the most efficient factor for the CO_2 corrosion in the oil producing wells.

There are 3 main elements in produced fluid; 1) Organic compounds such as grease, benzene, naphthalene and toluene. 2) Salts which primarily chlorides and sulfides. 3) Metal elements such as lead, chromium and nickel. In summary, produced waters are frequently one or all of the following:

a. hot
b. corrosive
c. oily, waxy
d. biologically active
e. contain solids
f. toxic

2.3.4 Solid Particle

Solids are also often present in produced fluids. They exist in many different forms, but principally originate from four individual sources:

a. Drilling mud debris
b. Reservoir sand
c. Scales (both organic and inorganic)
d. Corrosion products

Sand from the reservoir is the main contributor to the erosion corrosion in oil producing wells. CO_2 corrosion product, carbonate is one of the solid particles found in the produced fluids.

There are various types of corrosion that may occur in the oil producing well. Figure 1.6 below shows the components in typical oil producing well that are potential for corrosion to occur.

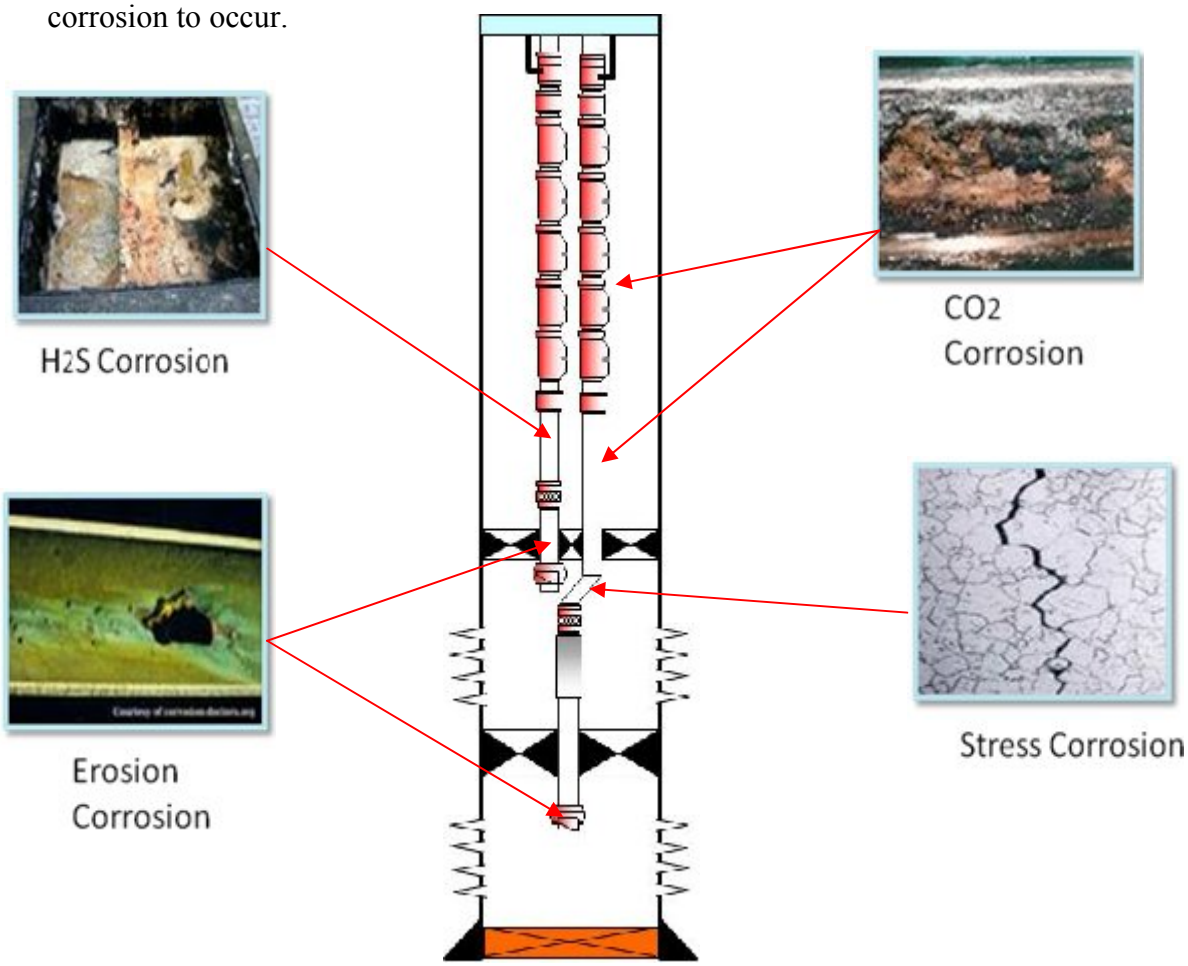


Figure 2.6: Types of Corrosion in Oil Producing Well

2.4 Basic of CO_2 Corrosion

Dry CO_2 gas by itself is not corrosive at the temperatures encountered within oil and gas production systems [8]. It becomes corrosive when dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase. Various mechanisms have been postulated for the CO_2 corrosion process but all involve either carbonic acid (H_2CO_3) or the bicarbonate ion ($2HCO_3^-$) formed on dissolution of CO_2 in water [10]. The step for the CO_2 corrosion process is presented by the reaction shown in the equations as follows:

$$CO_{2\,(aqueous)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (2.1)$$

The mechanism suggested by de Waard is:

$$H_2CO_3 + e^- \rightarrow H + HCO_3^- \quad (2.2)$$

$$2H \rightarrow H_2 \quad (2.3)$$

With the steel reacting:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (2.4)$$

The overall equation is:

$$CO_2 + H_2O + Fe \rightarrow FeCO_3 + H_2 \quad (2.5)$$

On the other hand, CO_2 corrosion results from the practice of pumping CO_2 saturated water into wells to enhance oil recovery and reduce the viscosity of the pumped fluid. The presence of CO_2 in solution leads to the formation of a weak carbonic acid which drives CO_2 corrosion reactions [10]. The initiating process is presented by the reaction shown in equation (2.6).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (2.6)$$

The following corrosion process is controlled by three cathodic reactions and one anodic reaction. The cathodic reactions, include (2.7a) the reduction of carbonic acid into bicarbonate ions, (2.7b) the reduction of bicarbonate ions, and (2.7c) the reduction of hydrogen ions

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \quad (2.7a)$$

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \quad (2.7b)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (2.7c)$$

The anodic reaction significant in CO_2 corrosion is the oxidation of iron to ferrous (Fe^{2+}) ion given in equation (2.8).

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (2.8)$$

These corrosion reactions promote the formation of $FeCO_3$ which can form along a couple of reaction paths. First, it may form when ferrous ions react directly with carbonate ions as shown in equation (2.9). However, it can also form by the two processes shown in equations (2.10a, 2.10b). When ferrous ions react with bicarbonate ions, ferrous iron bicarbonate forms which subsequently dissociates into iron carbonate along with carbon dioxide and water.

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \quad (2.9)$$

$$Fe^{2+} + 2HCO_3^- \rightarrow Fe(HCO_3)_2 \quad (2.10a)$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O \quad (2.10b)$$

CO_2 = Carbon Dioxide
H_2O = Water
H_2CO_3 = Carbonic Acid
Fe = Iron
$FeCO_3$ = Iron Carbonate (corrosion product)
H_2 = Hydrogen

The significance of $FeCO_3$ formation is that it drops out of solution as a precipitate due to its limited solubility. This precipitate has the potential to form passive films on the surfaces of steel which may reduce the corrosion. [9]

2.4.1 Types of CO_2 Corrosion Failure

In oil producing wells, CO_2 corrosion have always presented as a severe problem to the production tubing. Most of the cases, corroded tubing may deplete the production and need very high cost maintenance to rectify the problem [1]. In addition, the risk of pollution and hazards to safety are the important reasons for adequate further on corrosion study. Below are the lists of effect due to carbon dioxide corrosion to internal tubing surface:

a. Pitting

   Pitting is defined as corrosion of a metal surface, confined to a point or small area that takes the form of cavities [9]. Pitting can occur over the full range of operating temperatures under stagnant to moderate flow conditions. Pitting may arise close to the dew point and can relate to condensing conditions. The susceptibility to pitting increases and time for pitting occur decrease with increasing temperature and increasing CO_2 partial pressure.

b. Mesa type attack

   It is a form of localized CO_2 corrosion occurs under medium flow conditions where the formation of protective $FeCO_3$ film layers is unstable. Film formation begins around 60°C and thus mesa attack is much less of a concern at temperatures below this [9]. The type of this attack most encountered in the area which is has high fluid turbulence such as welds, tubing joints, or ends/constrictions in piping.

c. Flow induced localized corrosion (FILC)

   The damage is an extension of pitting and mesa attack above critical flow intensities. The localized attack propagates by local turbulence created by pits and steps at the mesa attack which act as flow disturbances. The local turbulence combined with these stresses inherent in the scale may destroy existing scales. The flow conditions may then prevent protective $FeCO_3$ film layers on the exposed metal to reform again.

2.4.2 CO_2 Corrosion Prevention Method

To know the fact that CO_2 corrosion phenomenon cannot be eliminated in oil producing wells, the only way to reduce the problem is to minimize as much as possible the effect and severity caused by CO_2 corrosion. The lists below are some of the CO_2 corrosion prevention method that are widely use in oil and gas industry.

a. Corrosion Inhibitor

A corrosion inhibitor is a chemical compound that, when added to a fluid or gas, decreases the corrosion rate of a metal or an alloy [15]. The corrosion inhibition efficiency of a corrosion inhibitor is a function of many factors such as fluid composition, quantity of water and flow regime. In oil producing wells, the oil itself may be the inhibitor if the produced fluids GOR is low. But in most of the cases, corrosion inhibitor such as hydrazine and ascorbic acids is injected into the production tubing periodically to decrease the corrosion rate.

b. Cathodic Protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell. Cathodic protection interferes with the natural action of the electrochemical cells that are responsible for corrosion [15]. Cathodic protection can be effectively applied to control corrosion of surfaces that are immersed in water.

c. Protective Coating

Protective coatings are the most widely used corrosion control technique. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur. However, the protective coatings can never provide 100 percent protection of 100 percent of the surface [15]. Coatings are particularly useful when used in combination with other methods of corrosion control such as cathodic protection.

2.5 Tests for CO_2 Corrosion

In order to study and analyze the CO_2 corrosion rate in API L-80 steel, two (2) methods of laboratory test are conducted.

2.5.1 Weight Loss Method using Autoclave

Weight loss measurement is the most widely used means of determining corrosion loss, despite being the oldest method currently in use [12]. A Weight sample (coupon) of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The coupon is then cleaned of all corrosion products and is reweighed. The weight loss is converted to a corrosion rate or metal loss. The technique requires no complex equipment or procedures, merely an appropriately shaped coupon, a carrier for the coupon (coupon holder), and a reliable means of removing corrosion product without disruption of the metal substrate.

The method is commonly used as a calibration standard for other means of corrosion monitoring, such as Linear Polarization Resistance Method. In instances where slow response and averaged data are acceptable, weight loss monitoring is the preferred technique. The Weight loss method tests are to be conducted using Autoclave Corrosion Test Equipment (refer to Figure 2.7) to determine the CO_2 corrosion rate in API L-80 steel.

Autoclave corrosion tests are a convenient means for laboratory simulation of many service environments for the purpose of evaluating corrosion resistance of materials and for determining the effects of metallurgical, processing, and environmental variables on corrosion processes. The reason for such tests is to more closely recreate the high temperature and pressure commonly occurring in commercial or industrial processes. In most situations involving aqueous corrosion, it involves a water-based solution containing various dissolved salts such as chlorides, carbonates, bicarbonates, alkali salts, acids and other constituents [7].

Using Autoclave, high temperature and high pressure corrosion test in static condition is possible to be conducted under the environment as mentioned above which is simulating the actual condition in oil producing well.

The Autoclave Corrosion Test Equipment is designed to specification given in the ASME Boiler and Pressure Vessel Code and meets the ASTM G 31, Practice for Laboratory Immersion Corrosion Testing of Metals standard.

Figure 2.7: Autoclave Corrosion Test Equipment

2.5.2 Linear Polarization Resistance Method

Linear Polarization Resistance Monitoring (LPR) technique is the most efficient way to measure corrosion rate [14]. It is the only corrosion monitoring method that allows corrosion rates to be measured directly in real time. This method is useful to rapidly identify corrosion upsets and initiates remedial action in water-based, corrosive environments.

In the typical LPR technique, a potential (typically of the order of 10-20 mV) is applied to a freely corroding sensor element and the resulting linear current response is measured [16]. This small potential perturbation is usually applied step-wise, starting below the free corrosion potential and terminating above the free corrosion

potential. The polarization resistance is the ratio of the applied potential and the resulting current response. This resistance is inversely related to the uniform corrosion rate.

The corrosion current $I_{corr,}$ generated by the flow of electrons from anodic to cathodic sites, could be used to compute the corrosion rate by the application of a modified version of Faraday's Law:

$$C - \frac{I_{CORR} \, x \, E}{A \, x \, D} \; x \; 128.67 \qquad (3.1)$$

where:

C = Corrosion rate in "mils per year" (MPY)

E = Equivalent weight of the corroding metal (g)

A = Area of corroding electrode (cm2)

d = Density of corroding metal (g/cm3)

Anodic and cathodic sites continually shift position, and they exist within a continuously conductive surface, making direct measurement of I_{corr} impossible [16]. Small, externally-imposed, potential shifts (ΔE) will produce measurable current flow (ΔI) at the corroding electrode. The behavior of the externally imposed current is governed, as is that of I_{corr}, by the degree of difficulty with which the anodic and cathodic corrosion processes take place.

From the linear polarization resistance test, we can determine the corrosion rate of the sample. The theory behind corrosion rate calculation is as mention below. The corrosion current density is related to polarization resistance by Stern_Geary coefficient, B. The Stern-Geary Constant, B, is approximated as 25 mV for all pH.

$$i_{corr} = B/R_p \qquad (3.2)$$

The dimension of R_p is ohm-cm2, i_{corr} is mA/cm^2, and B is in V. B also can be written as:

$$B = \frac{b_a \, b_c}{2.303(b_a \; | \; b_c)} \qquad (3.3)$$

Where ba, bc is the Tafel slope for cathodic and anodic reaction. According to the soft ware that we are using in the lab to do the calculation, Tafel Slope, B used in the calculation is 26.

The corrosion rate, CR in mm/year can be determined from the formula shown below:

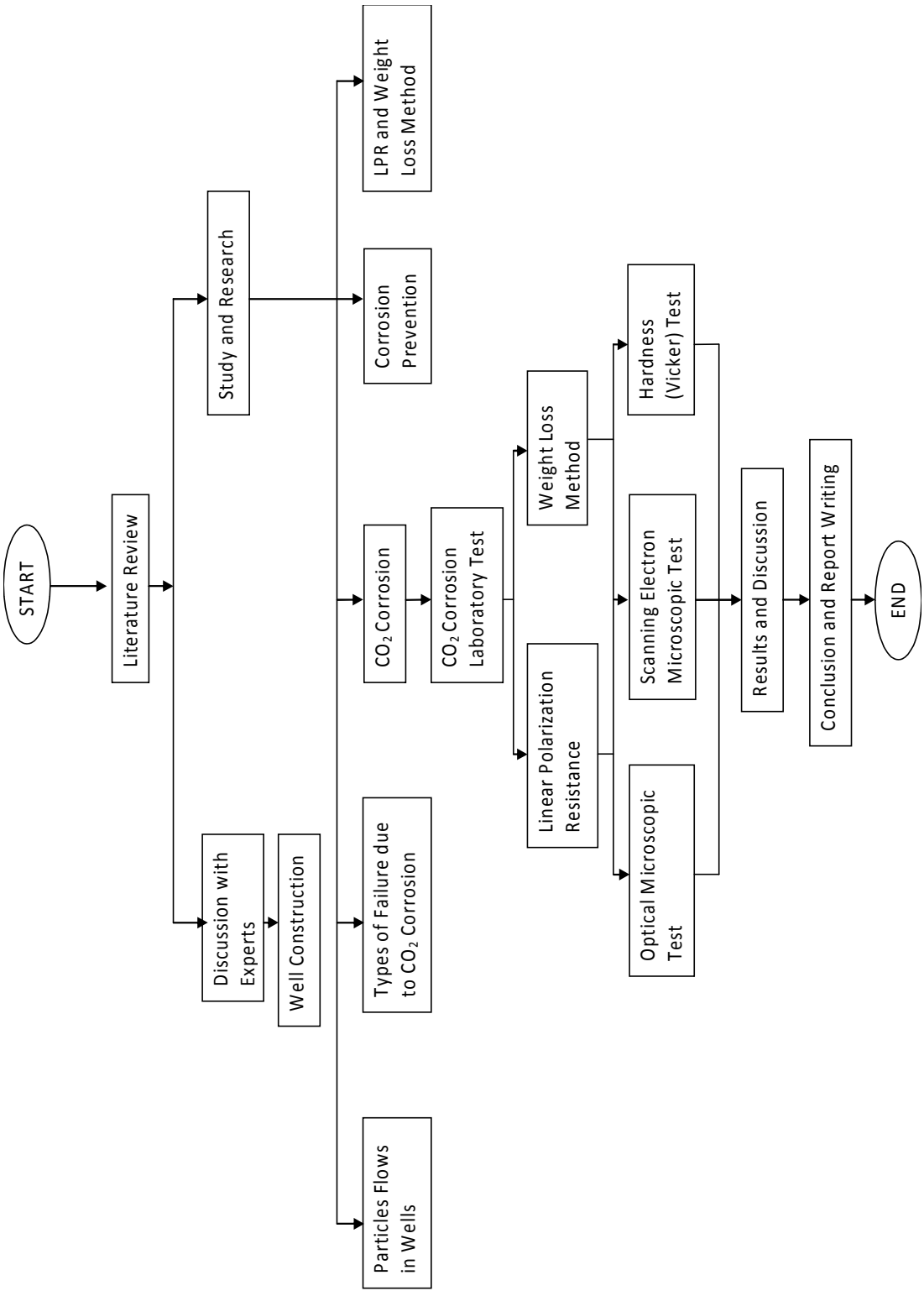
$$CR = 3.27 \times i_{corr} EW / \text{density of the corroding material} \quad (3.4)$$

where,
EW = equivalent weight of the corroding species in grams

CHAPTER 3

METHODOLOGY

3.1 Overall Project Flowchart



3.2 Weight Loss Method using Autoclave

A weighed sample, L-80 steel specimen was introduced into the process, and later removed after a reasonable time interval. The specimen was then cleaned of all corrosion products and reweighed. The weight loss was converted to a corrosion rate (CR) or metal loss (ML), as follows:

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (g)} \times K}{\text{Alloy Density (g/cm}^3\text{)} \times \text{Exposed Area (A)} \times \text{Exposure Time (hr)}}$$

Table 3.1: The constant values to calculate the corrosion rate in various units

Desired Corrosion Rate Unit (CR)	Area Unit (A)	K-Factor
mils/year (mpy)	in^2	5.34×10^5
mils/year (mpy)	cm^2	3.45×10^6
millimeters/year (mmy)	cm^2	8.76×10^4

$$\text{Metal Loss (ML)} = \frac{\text{Weight loss (g)} \times K}{\text{Alloy Density (g/cm}^3\text{)} \times \text{Exposed Area (A)}}$$

Desired Metal Loss Unit (ML)	Area Unit (A)	K-Factor
mils	in^2	61.02
mils	cm^2	393.7
millimeters	cm^2	10.0

Cleaning of specimens before weighing and exposure was critical to remove any contaminants that could affect test results [13]. Reference was made to NACE Recommended Practice RP-0775 and ASTM G-1 & G-4 for further detail on surface finishing and cleaning of weight-loss coupons. The experiments are to be conducted in Block I using Autoclave Corrosion Test Equipment using ASTM G-31, Practice for Laboratory Immersion Corrosion Testing of Metals as the reference.

3.2.1 Preparation of Specimen/Coupon

The material used for the experiment (L80 steel) was supplied by PETRONAS Carigali Sdn. Bhd. (PMO). The chemical composition of alloys as obtained from the company data sheet are as shown in Table 3.1. The steel was cut and machined using wire cut method in lab into the rectangular specimens of dimension 15 x 10 x 5mm and 3mm diameter of hole was cut at the center (refer to Figure 3.1) to facilitate suspension of the sample inside the Autoclave.

All faces of the samples were initially coarsed ground on SiC belt grinder machine then consequently machine polished to 800-grade finish using silicon carbide paper. The polished samples were washed and subsequently washed in acetone. 15 sets of specimens were prepared for the test.

Table 3.2: Chemical Composition of API L-80 Specimen

GRADE	C	Mn	Si	S	P	Cr	Mo
L-80	0.22	1.38	0.22	0.21	0.28	0.013	0

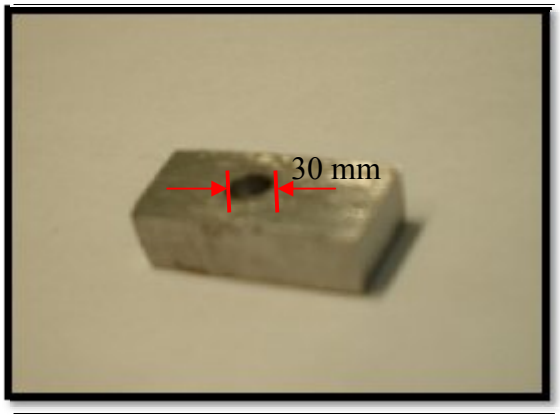


Figure 3.1: L-80 Steel Specimen for Weight Loss Method using Autoclave

3.2.2 Preparation of Solutions

The solutions were prepared from the 1 litre of deaerated water mixed with NaCl to achieve the 3% NaCl solution. The pH of the solution was adjusted to the pH=5. The pH value was checked by microcomputer pH-meter METTLER-TOLEDO Model 320, which had been calibrated using standard buffer.

3.2.3 Laboratory Setup

The set-up for the Weight loss laboratory test using Autoclave was showed in Figure 3.2 and Figure 3.3. The test assembly consists of Autoclave equipment, CO_2 gas supplier and a computer for data acquisition.

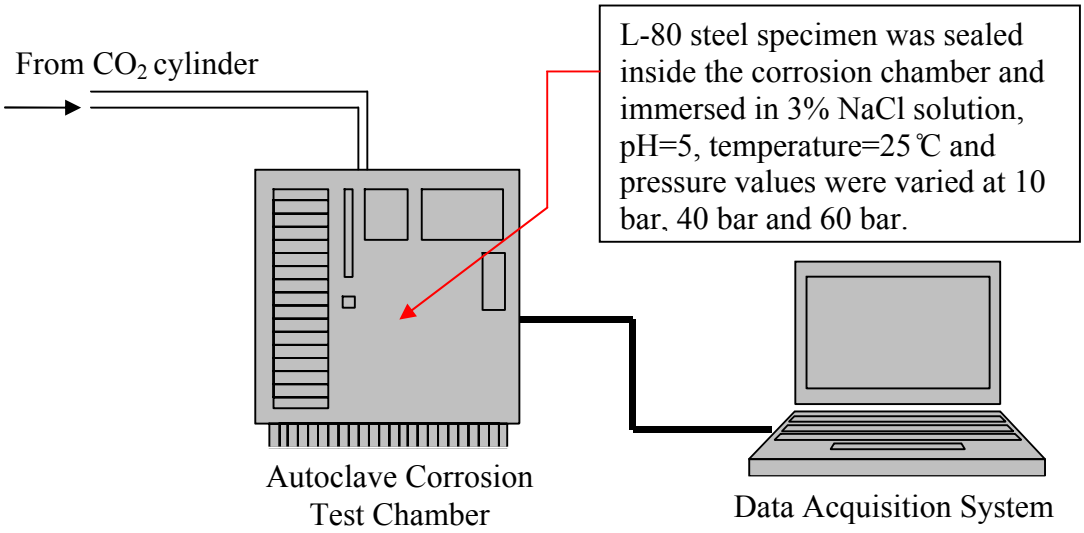


Figure 3.2: Schematic Diagram for Weight Loss Method using Autoclave

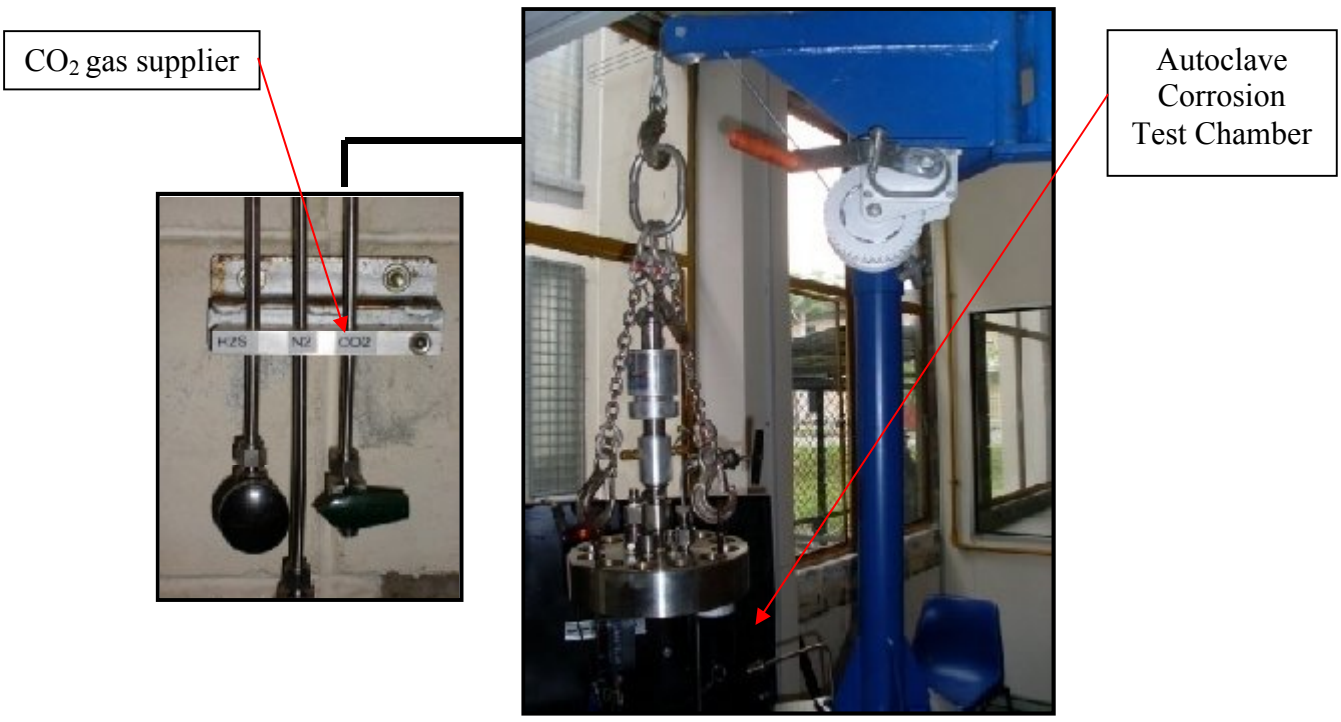


Figure 3.3: Real Weight Loss Method using Autoclave Test Setup

3.2.4 Experiment Procedures for Weight Loss Method using Autoclave

The temperature of solution used was constant at room temperature, 25 ℃. The pressure during the experiment was varied from 10 to 60 bar which is in the range of actual pressure condition in oil producing well (Tukau 45L) as provided by Production Technologist of PETRONAS Carigali Sdn. Bhd. The pressure value was controlled from the computer. The values of pressure of the solution used were:

a. 10 bar
b. 40 bar
c. 60 bar

Experiments procedures were as per described below:

a. Test solution and the test specimen were prepared as mentioned above. 1 liter of test solution where the temperature was maintained at 25 ˚C within 1℃ was prepared 1 hour before run the experiment.

The specimen prepared as per describe in Section 3.2.1 and setting up of the equipment for the laboratory test as per describe in Section 3.2.3.

b. Initial weights of the samples were measured using microbalance equipment. The average value of each sample was noted.
c. The Autoclave corrosion chamber was deaerated by using a pump vacuum and purging argon continuously for 1 hour to remove the oxygen impurity.
d. Then, the test solution was poured into the AutoClave corrosion chamber.
e. Three sets of coupons were placed hanging in the chamber to avoid any contact with any material that may caused galvanic caorrosion.
f. The chamber was then sealed using bolts and nuts.
g. The pressure was raised to 10 bar by charging CO_2 gas into the chamber. The process was controlled by the digital display unit (DDU) in the computer. SmartCET software from Honeywell was used to control and for data acquisition during the experiment.
h. The experiment was kept running for 48 hours continuously.
i. Experiment for 40 bar and 60 bar pressure were conducted using the same procedure as mention above.
j. In order to analyze the corrosion products, scanning electron microscopic (SEM) was used on the coupons after each of the experiment.
k. Micro hardness test was conducted later to measure the effect of CO_2 corrosion to the coupons.

3.3 Linear Polarization Resistance Method

Linear Polarization Resistance Method was used to determine the corrosion rate of metal in a specific environment. ASTM 59, Standard Method in Conducting Potentiodynamic Polarization Resistance Measurements described the experimental procedure for polarization resistance method which can be used for calibration of equipment and verification of experimental technique.

The test method can be utilized to verify the performance of polarization resistance measurements equipments. Polarization resistance can be related to the rate of general corrosion for metal at or near the corrosion potential, it is an accurate and rapid way to measure the general corrosion rate. The test procedures standard included were:

a. Test solutions were prepared, and the standard test cell requires 900ml of test solution where the temperature was maintained at 30 ˚C within 1℃.
b. Test cell was purged at 150 cm^3 /min before specimen immersion and continue throughout the test.
c. Working electrode was prepared, and experiment was conducted within 1 hour of the preparing electrode. Preparation including sequential wet polishing with 240 grit and 600 grit SiC paper. Surface area of the specimen was determined to the nearest of 0.01 cm^2 and subtract the area under the gasket.
d. Prior to immersion of the specimen, it was degreased with acetone and rinsed with distilled water. The time delay between rinsing and immersion was kept minimal.
e. The test specimen was transferred into test cell and position the probe trip to 2 to 3 mm from the test electrode surface. The diameter of the tip was not more than 1 mm.

3.3.1 Preparation of the Working Electrode

The samples (L80) were cut into 2cm diameter cylinder and spot welded with copper wire. Then, it was mounted with epoxy by cold mounting and then polished to 800-grade finish using silicon carbide paper. Finally, it was degreased and rinsed with deionizer water and ethanol. The working electrode is as shown below.

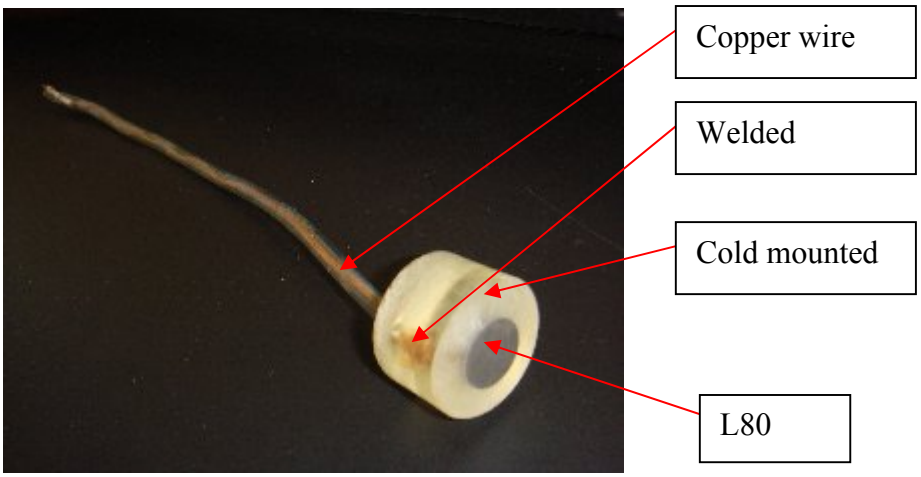


Figure 3.4: Working Electrode used in the LPR Test

3.3.2 Preparation of Solutions

The solutions were prepared from the 3% NaCl solution was saturated with CO_2 by purging for one hour prior to the exposure of electrode. The pH of the solution was adjusted by adding an amount of sodium hydrogen carbonate. The pH value was checked by microcomputer pH-meter METTLER-TOLEDO Model 320, which had been calibrated using standard buffer.

3.3.3 Laboratory Setup

The set-up for the laboratory test using electrochemical measurement using linear polarization resistance method is showed below. The test assembly consist of one liter glass cell bubbled with CO_2 gas. The required test temperature was set through hot plate. The electrochemical measurements were based on a three-electrode system. The reference electrode used was a saturated calomel electrode (SCE) and the auxiliary electrode was a platinum electrode. Figure 3.5 shows the schematic diagram of the test and Figure 3.6 shows the real test setup in laboratory.

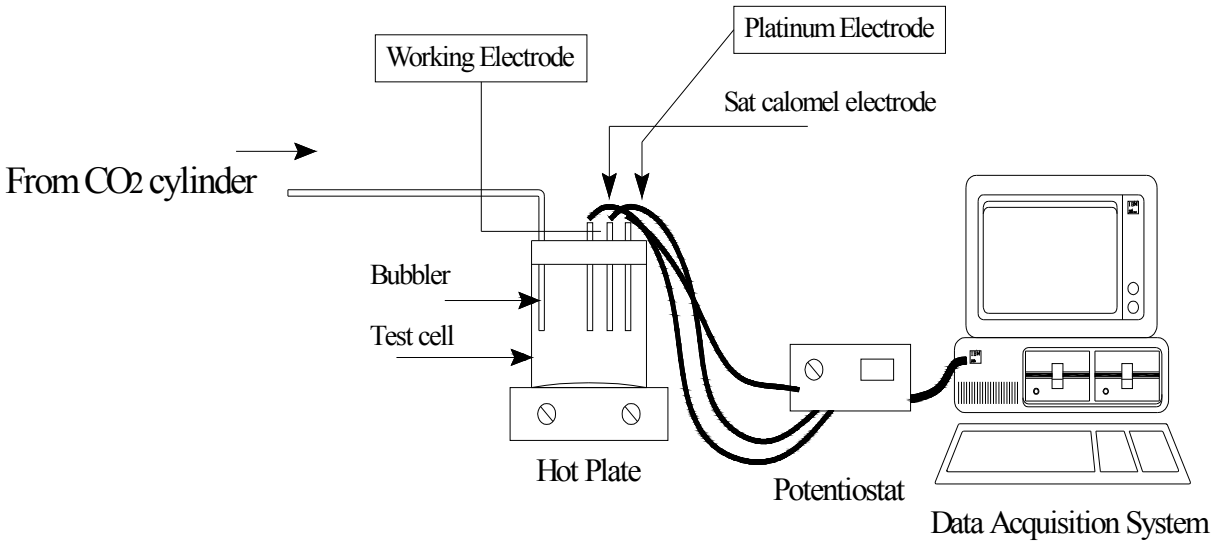


Figure 3.5: Schematic Diagram of LPR Test

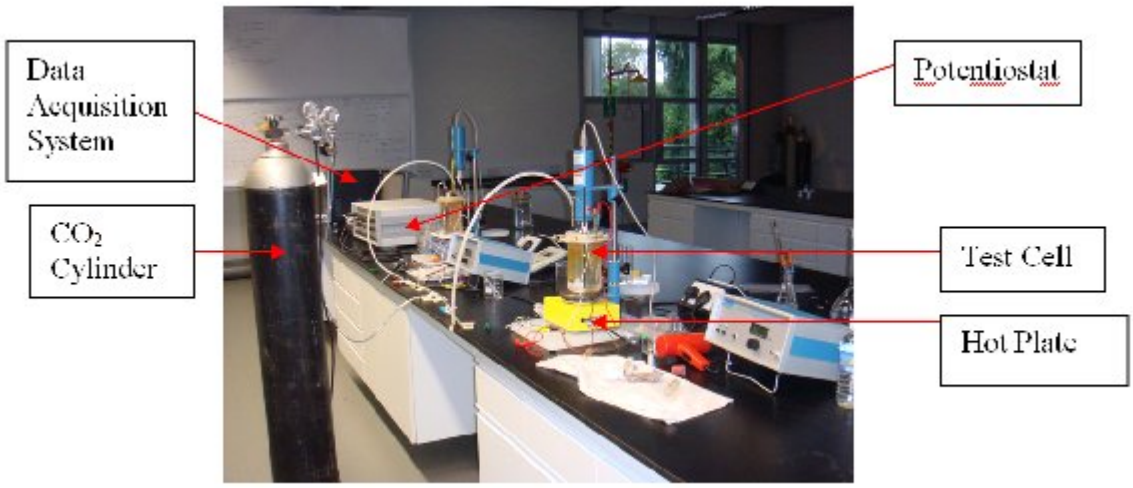


Figure 3.6: Real LPR Test Setup in Laboratory

3.3.4 Experiment Procedures for Temperature and Rotational Rate Parameters using LPR

The temperature of solution used was varied from 60 to 120 ˚C. The rotational rate during the experiment was varied from 0 to 6000 rpm. The pressure was constant at atmospheric pressure, 1 atm. The temperature values and the rotational rate values were within the range of actual condition in oil producing well (Tukau 45L) as provided by Production Technologist of PETRONAS Carigali Sdn. Bhd. Hot plate was used to control the temperature at constant value throughout the experiment. The values of temperature of the solution used were:

a. 25 °C
b. 40 °C
c. 60 °C

The values of rotational rate used were:

a. 0 rpm
b. 1000 rpm
c. 2000 rpm
d. 4000 rpm
e. 6000 rpm

Experiments procedures were as per described below:

a. Solution medium of sodium chloride 3% prepared, 30g of sodium chloride was mixed into the distilled water of 1 liter.
b. Working electrode prepared as per describe in the Section 3.3.1 and setting up of the equipment for the laboratory test as per described in Section 3.3.3.
c. Purging of the carbon dioxide gas started and continuous purging for half an hour until the carbon dioxide was saturated in the solution. The indication of the cell was saturated with carbon dioxide was tested with the pH meter when it indicated the reading of pH nearly 3.8.
d. The solution was then heated up to 25^{o}C to provide the desired temperature for the experiment, and sodium bicarbonate was added into the solution to increase the pH of the solution to 5. The pH value was constant throughout the experiment for temperature parameter. Once, the environment of the experiment achieved.
e. For the first section of the experiment, the solution was maintained at 25°C at rotational rate 0 rpm. After one hour of test run, the result yielded from the experiment was noted and run for another hour. This procedure was repeated for the rotational rate value at 1000 rpm, 4000 rpm and 6000 rpm. Proceed to step (h).
f. Second section of the experiment was using 40°C as the solution temperature and rotational rate at 0 rpm. The hot plate was set at 40°C and then maintained on the test run for 1 hour. The results and output graph yield for the next 1 hour was noted. This procedure was repeated for the rotational rate value at 1000 rpm, 4000 rpm and 6000 rpm. Proceed to step (h).
g. Third section of the experiment was using 60°C as the solution temperature and rotational rate at 0 rpm. The hot plate was set at 60°C and then maintained on the test run for 1 hour. The results and output graph yield for the next 1 hour was noted. This procedure was repeated for the rotational rate value at 1000 rpm, 4000 rpm and 6000 rpm. Proceed to step (h).
h. Once the working electrode was added into the solution, the data acquisition system yielded the results. Then, Gill 12 Weld Tester Serial No. 1350 – Sequencer and the Core Running software was run.

i. Then, ACM Instruments was run and data was gathered automatically into the ACM Analysis, where it recorded down the Linear Polarization Resistances and calculated the corrosion rate using the formula.

3.4 Scanning Electron Microscopic (SEM)

The SEM test was conducted to analyze the corrosion products at the specimens after each experiment. The SEM machine is attached with EDM equipment where the chemical composition of the L-80 steel can be detected. All of the specimens were sealed and sent to the SEM lab within 1 hour prior to the test. The test was conducted by lab technician in UTP Academic Block, Building 17 because of the high cost and high radiation emitted during the test.

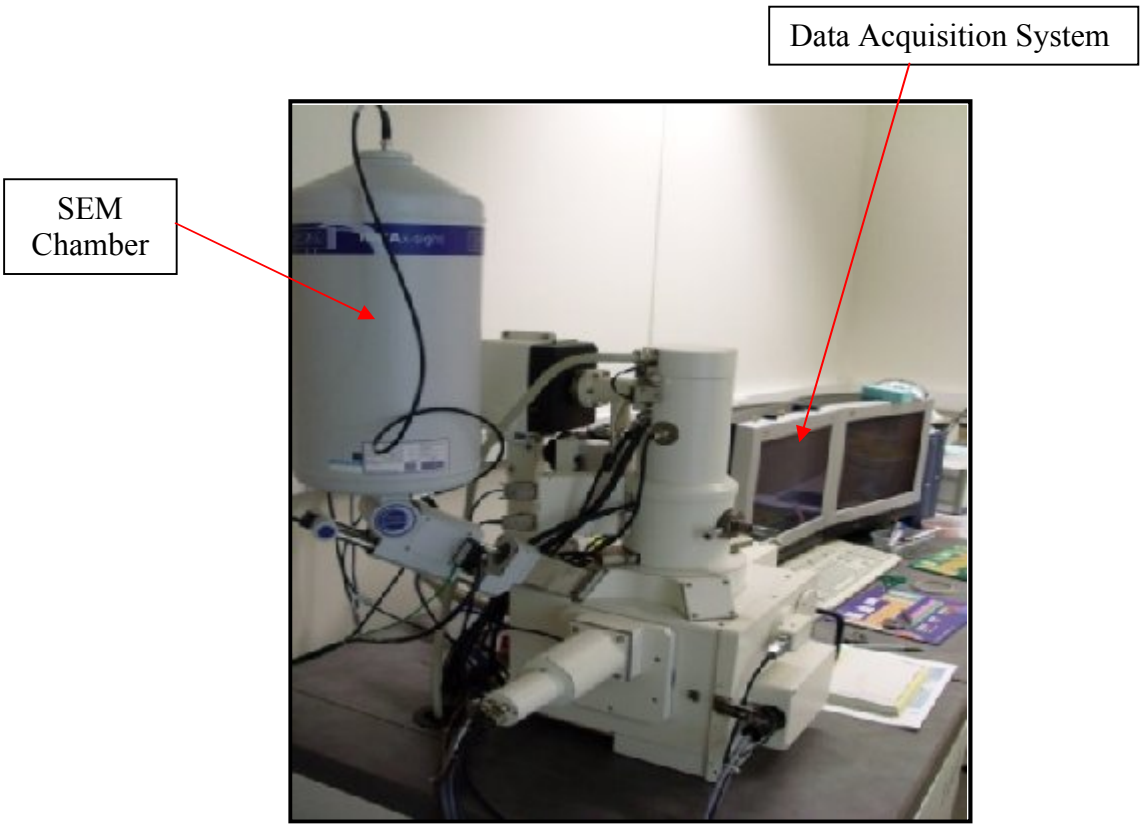


Figure 3.7: SEM Machine

3.5 Optical Microscopic Test

Optical Microscopic Test was conducted to analyze the surface condition of the specimens after each experiment. The tests procedures were as shown below:

a. After completed the Weight Loss Method, Linear Polarization Method and SEM test, the specimens were sealed in vacuum.
b. The specimens were cleaned with ethanol.
c. Then, nital (etchant) was used to the specimens prior to 1 minute before conducting optical microscopic test.
d. The surface condition of each specimen was recorded by a computer for data acquisition.

3.6 Microhardness (Vicker) Test

The test was conducted to analyze the effect of CO_2 corrosion to the hardness of the material. The specimen's microhardness was tested before and after corrosion. The parameters used during the test are as shown below:

a. Test Load = 50 gf
b. Dwell Time = 15 seconds

The test procedures were as mentioned below:

a. The test specimens were mounted using the Auto Mounting Press Machine to achieve a flat surface as a requirement to conduct the Microhardness Test.
b. Then, the flat face of the specimens were coarse ground on SiC belt grinder machine until 1200 grit silicon carbide paper and consequently polished using 6 grade and 1 grade diamond paste.
c. The specimens were washed using ethanol and prepared for the test.
d. The specimen was placed under a microscope and positioned until it shows the grain structure of the material. 50 gf load test was applied to the specimen until a 'diamond shaped' on the surface can be seen from the microscope.
e. The length of the diamond hole was measured and the Microhardness Test Machine automatically calculated the material's hardness in HV units.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Actual Data from Tukau 45L Oil Producing Well

To conduct the tests based on actual condition in oil producing well, the author managed to receive some data from PETRONAS Carigali Sdn. Bhd (SKO). Tests conducted were to simulate the actual condition of Tukau 45L oil producing well in Tukau Field, Sarawak. The oil is producing from the 2-F6/G2 reservoir. Table 4.1 shown below is the results from the Flowing Gadient Survey that was conducted at the oil producing well on 6th October 2008 using wireline operation. Figure 4.1 and Figure 4.2 below show that the value of temperature and pressure during the production. The data provided was used as a reference to the value of parameters used during the experiment.

Table 4.1: Data Acquired from FGS Operation in Tukau 45L Well

FLOWING GRADIENT SURVEY

FIELD	: **TUKAU**	**START OF SURVEY**	:	6/10/2008	
WELL	: **TK 45L**	**DERRICK FLOOR ELEVATION**	:	92.0	**FT. AMSL**
RESERVOIR	: **2-F6/G2**	**TOP BOTTOM FLANGE**	:	50.0	**FT. BDF**
		PERFORATIONS	:	3088' - 3199'	**FT. BDF**

	AH DEPTH (FT BDF)		TV DEPTH (FT SS)	CORRECTED TV DEPTH (FT SS)	TEMP (DEG F)	PRESSURE (PSIA)		GRADIENT (PSI/FT. SS)	
	L.E	*	L.E	L.E		U.E.	L.E.	U.E.	L.E.
1st lubr.	50.0		-42.0		96.7	124.3	124.7		
flw. grad	465.0		372.8		118.1	163.5	164.6	0.094	0.096
flw. grad	665.0		572.6		119.7	180.9	180.8	0.087	0.081
flw. grad	865.0		772.5		121.2	192.5	193.6	0.058	0.064
flw. grad	885.0		792.5		121.5	205.8	205.3	0.665	0.585
flw. grad	1195.0		1101.9		123.5	233.9	234.8	0.091	0.095
flw. grad	1505.0		1407.9		125.3	268.7	268.8	0.114	0.111
flw. grad	1525.0		1427.4		125.4	270.7	270.2	0.103	0.072
flw. grad	1740.0		1634.8		126.3	295.4	295.1	0.119	0.120
flw. grad	1960.0		1844.3		127.2	323.8	324.2	0.136	0.139
flw. grad	1980.0		1863.3		127.6	327.4	327.0	0.189	0.147
flw. grad	2490.0		2353.5		132.9	513.1	512.2	0.379	0.378
flw. grad	2960.0		2794.3		136.7	686.8	686.0	0.394	0.394
flw. grad	3065.0		2889.6		136.9	725.9	725.9	0.410	0.419
flw. grad	3100.0		2921.3		136.9	737.9	737.4	0.378	0.363
2nd lubr.	50.0		-42.0		104.1	132.7	133.9	0.204	0.204

* DEPTH U.E. = (DEPTH L.E. - 2.0) FT

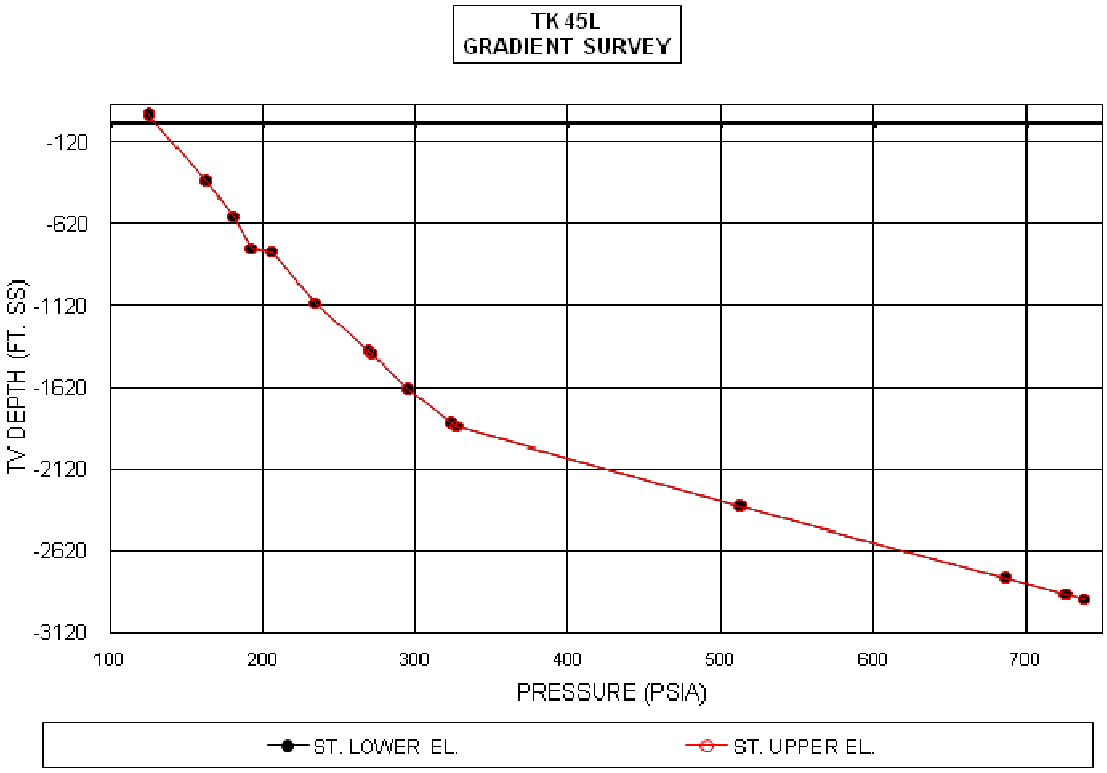


Figure 4.1: Depth vs. Pressure Graph for Tukau 45L Well

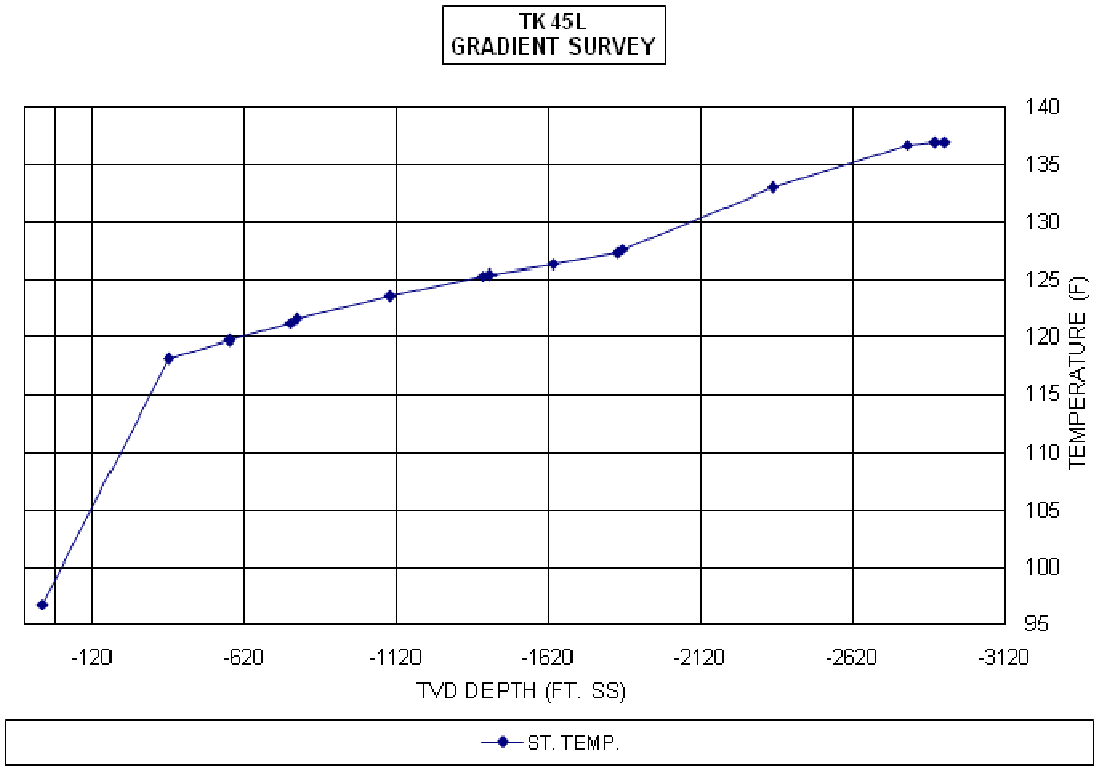


Figure 4.2: Temperature vs. Depth Graph for Tukau 45L Well

Laboratory tests were conducted using the data above. The test matrixes for each test are as shown below. All tests were using API L-80 steel specimen.

a. Laboratory experiment to determine the CO_2 corrosion rate in L80 steel under static condition using Autoclave Weight Loss Method with varied pressure (10 bar, 40 bar and 60 bar), in 3% NaCl solutions, at room temperature (25˚C) and pH5. Pressure value from Tukau 45L oil producing well; 100 to 750 psi which is approximately equals to 7 to 51 bar.
b. Laboratory experiment to determine the CO_2 corrosion rate in L80 steel using Linear Polarization Method with varied temperature (25˚C, 40˚C and 60˚C) and varied rotational rate (0 rpm, 1000 rpm, 2000 rpm, 4000 rpm and 6000 rpm), in 3% NaCl solutions, at atmospheric pressure (1 atm) and pH5. Temperature value from Tukau 45L oil producing well; 95 to 140 Fahrenheit which is approximately equals to 35 to 60℃.
c. Laboratory experiment to analyze the corrosion product and surface condition before and after corrosion occurs, SEM and OM test.
d. Laboratory experiment to analyze the effect of CO_2 corrosion on the material's hardness.

4.2 Weight Loss Method using Autoclave Test Results

Three sets of experiments with two specimens each were conducted. The first experiment was conducted at 10 bar pressure environment. The second experiment was conducted at 40 bar pressure and the third experiment at 60 bar pressure environment. Table 4.2 below shows the average weight different (gram) of the specimens with the respective pressure.

Table 4.2: Average Weight Differences in API L-80 Steel Specimens

	10 bar	40 bar	60 bar
Specimen 1 (gram)	0.0055	0.0093	0.0096
Specimen 2 (gram)	0.006	0.0082	0.011

Based on the theory explained in the previous section, the corrosion rate is calculated by the formula:

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (g)} \times K}{\text{Alloy Density (g/cm}^3\text{)} \times \text{Exposed Area (A)} \times \text{Exposure Time (hr)}}$$

where:

L80 steel density = 7.86 g/cm^3

Exposed area = 5.5 cm^2

Exposure time = 48 hours

K = 8.76 x 10^4

The average CO_2 corrosion rate in tubing steel (API L-80) at 10 bar, 40 bar and 60 bar, in 3% NaCl solutions, at room temperature (25℃) and solution pH5 using Autoclave Weight Loss method is shown as per Table 4.3 below:

Table 4.3: Average CO_2 Corrosion Rates in API L-80 Steel from Weight Loss Method Test

	Corrosion rates (mm/yr)	
Pressure	Specimen 1	Specimen 2
10 bar	0.2334	0.254
40 bar	0.3905	0.347
60 bar	0.4044	0.4681

4.2.1 Weight Loss Method Test: Discussion

The experiment was conducted in static condition, immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 10 bar, 40 bar and 60 bar and temperature is constant throughout the experiment at 25°C. The L 80 steel corrosion rate yields from the experiment is in the range of 2.3 x 10^3 to 4.7 x 10^3 mm/yr.

The trend is increasing with the increase of pressure values. It is known that in high pressure environment, the corrosion rate will increase due to local depletion of HCO_3^- ions which is favoring the cathodic reaction that can lead to corrosion.

The analysis on the specimen surface condition after the tests is discussed in Section 4.4 and Section 4.5 under the SEM and OM tests results.

4.3 Linear Polarization Resistance Method Tests Results

Based on the theory explained in the previous section, the corrosion rate is calculated by the data acquisition system using software called Gill 12 Weld Tester Serial No 1350- Sequencer. The corrosion rate result of the L80 steel at varied temperature (25℃, 40 ˚C and 60℃) and varied rotational rate (0 rpm, 1000 rpm, 2000 rpm, 4000 rpm and 6000 rpm), in 3% NaCl solutions, at atmospheric pressure (1 atm) and solution pH5 is shown in Table 4.4 and Figure 4.3.

Table 4.4: Average CO_2 Corrosion Rates in API L-80 Steel from LPR Test

Temperature (˚C)/ Rotational Rates (rpm)	Average CO2 Corrosion Rates (mm/yr)		
	at 25˚C	at 40˚C	at 60˚C
0	1.35	2.26	2.9
1000	1.44	2.31	3.14
2000	1.7	2.35	3.68
4000	2.03	2.41	3.85
6000	2.14	2.59	3.9

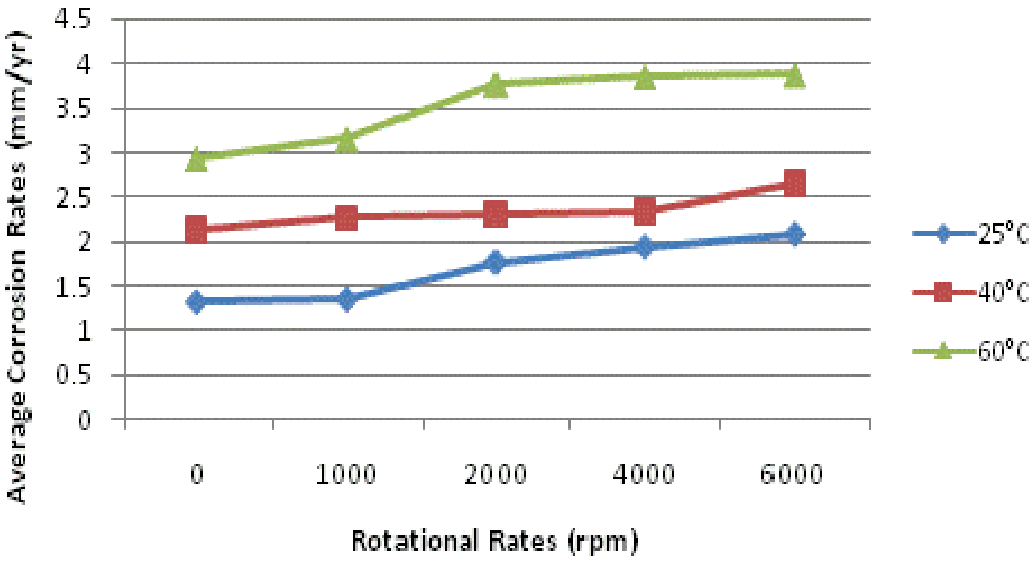


Figure 4.3: Average CO_2 Corrosion Rates from LPR Test at Different Rotational Rates and Different Temperature

4.3.1 Linear Polarization Resistance Method Test: Discussion

The API L-80 steel corrosion rate yields from the experiment are in the range of 1.3 to 3.9 mm/year. At low temperature (25˚C to 40℃) and rotational rates = 0 rpm, the corrosion rate of samples shows a significant increasing trend from 1.35 mm/yr to 2.26 mm/yr. This is due to the continuous dissolution of Fe^{2+} ions as a result of formation of porous $FeCO_3$, which is not protective in nature. However, as the temperature increases from 40 ˚C to 60℃, the $FeCO_3$ layer become less porous, more adherent to the L 80 steel surface and protective in nature. Hence, the corrosion rates only increase from 2.26 to 2.90 mm/yr. At higher temperature (above 60 ˚C), the $FeCO_3$ is more stable thus protecting the surface from corrosion.

The corrosion rate is increasing significantly when the rotational speed was introduced to the specimens. This is due to the formation of $FeCO_3$ protective layers were washed away by the fluid velocity. The effect can be seen more clearly at the low temperature (25 ˚C) experiment where the $FeCO_3$ layer is more porous. The corrosion rates increased from 1.75 mm/yr at 1000 rpm rotational rates to 2.14 mm/yr at 6000 rpm rotational rates.

The average corrosion rates yield from LPR test is higher than the average corrosion rates yield from Weight Loss Method test. This is due to the short period of LPR test since the corrosion rates were monitored on-time and the data was taken on every 5 minutes intervals for 15 readings. During these 75 minutes, the CO_2 corrosion rate of the L-80 is increasing significantly. However, as the time passed, the corrosion rate is still increasing but at a slower trend due to the formation of $FeCO_3$ protective layer on the surface. Figure 4.4 shows the typical CO_2 corrosion rates trend in aqueous solution.

For the Weight Loss Method, the test was conducted for 48 hours. Thus, the average CO_2 corrosion rates yield from the test is lower than LPR test due to the protective $FeCO_3$ layer formed on the specimen surface.

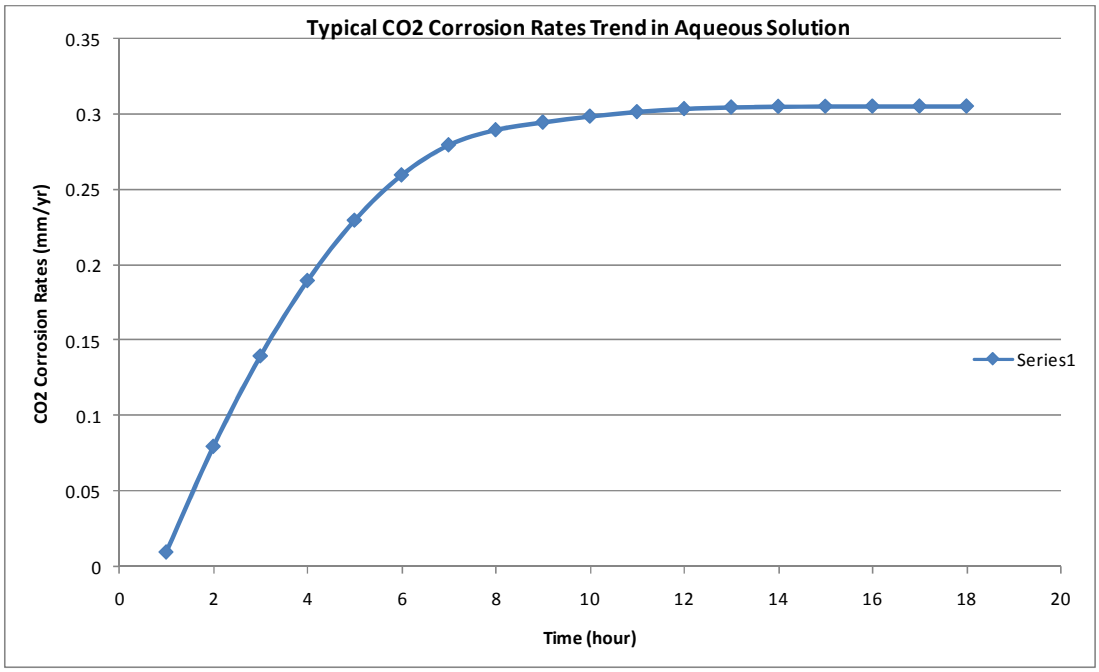


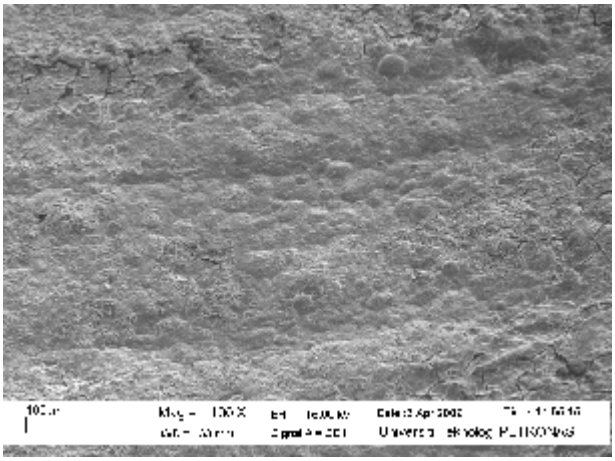
Figure 4.4: Typical CO_2 Corrosion Rates Trend in Aqueous Solution

4.4 Scanning Electron Microscopic Tests Results

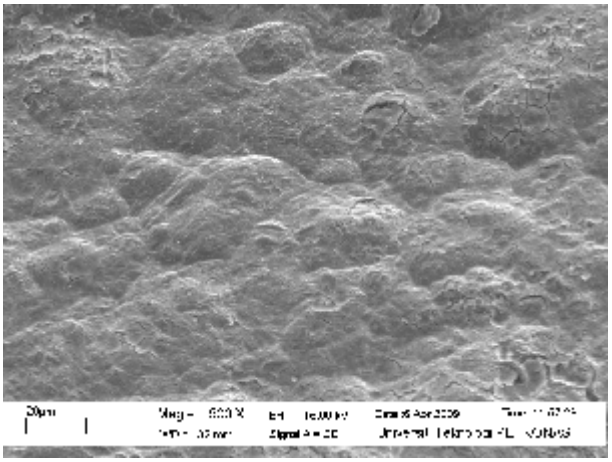
All the specimens were taken to SEM Laboratory after the Weight Loss Method Tests. The test was conducted to understand the micro level aspect of the CO_2 corrosion product in API L-80 steel specimen before and after corroded. The image shows the CO_2 corrosion product and the formation of $FeCO_3$ layer on the L 80 steel surface. The SEM Tests were conducted on four different L-80 steel specimens:

a. SEM image of the initial L-80 steel that not-affected with any electrochemical reaction in different magnification
b. SEM image of L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 10 bar and temperature of 25°C in different magnification
c. SEM image of L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 40 bar and temperature of 25°C in different magnification
d. SEM image of L 80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 60 bar and temperature of 25°C in different magnification

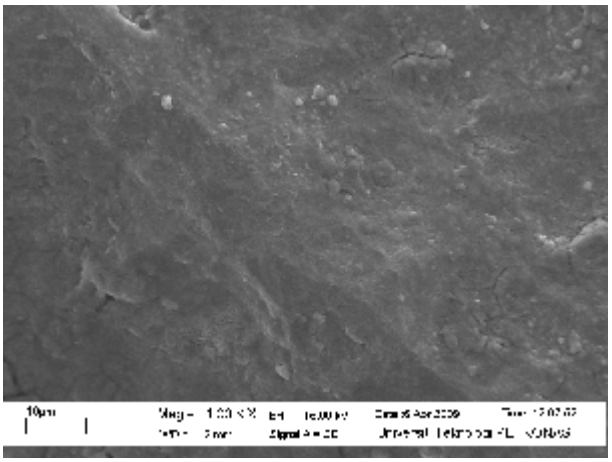
4.4.1 API L-80 Steel



(a)



(b)

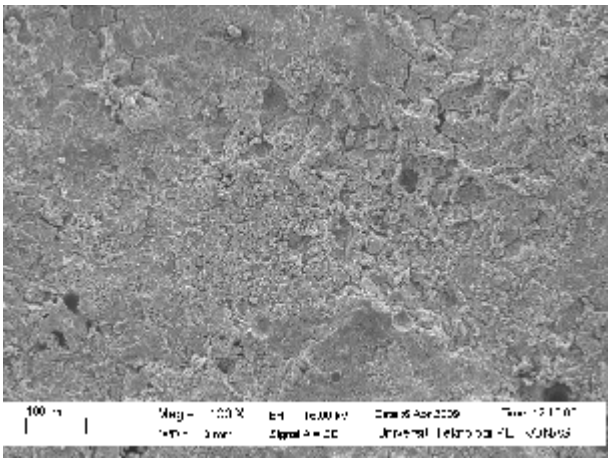


(c)

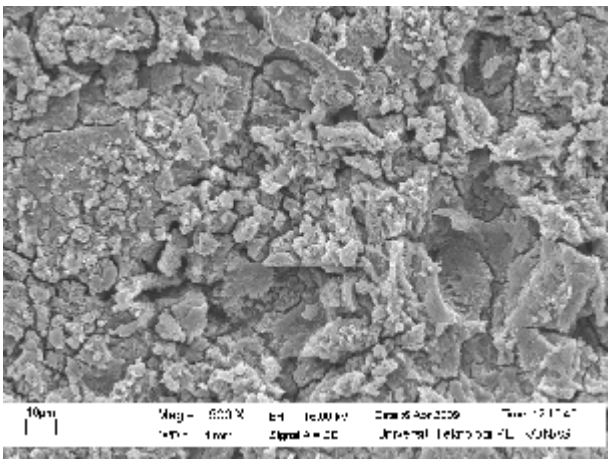
Figure 4.5: SEM micrographs of L-80 steel that not-affected with any electrochemical reaction. (a) 100x (b) 500x (c) 1000x

The SEM micrographs above show the initial surface condition of API L-80 steel specimen before being tested in CO_2 corrosion environment. The surface was fairly smooth without any sign of holes, crack or corrosion products.

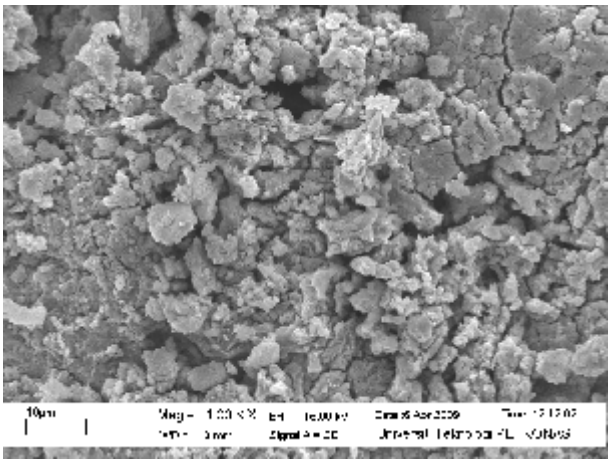
4.4.2 API L-80 Steel after 48 hours immersed in 3% NaCl solutions pH 5, at pressure 10 bar and temperature 25˚C.



(a)



(b)

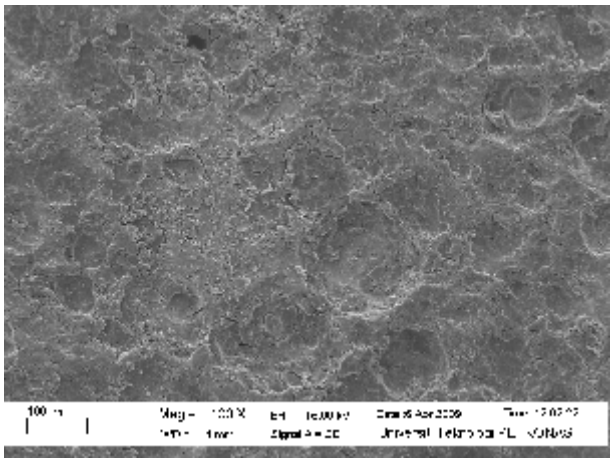


(c)

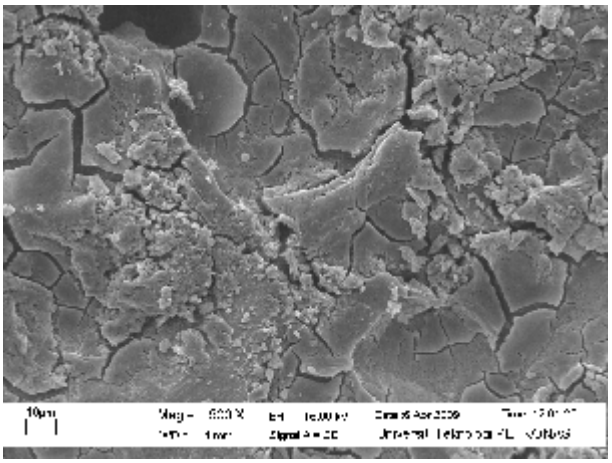
Figure 4.6: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH=5, at pressure of 10 bar and temperature 25℃ (a) 100x (b) 500x (c) 1000x

The SEM images show the corrosion products, $FeCO_3$ film layers formed were porous due to the fact that the experiment was conducted at low temperature (25℃).

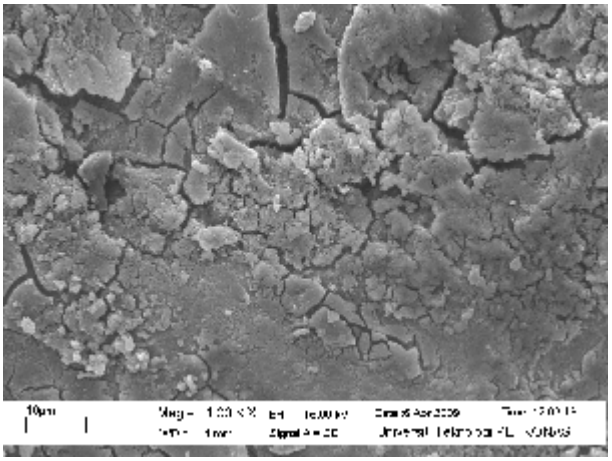
4.4.3 API L-80 Steel after 48 hours immersed in 3% NaCl solutions pH 5, at pressure 40 bar and temperature 25˚C.



(a)



(b)

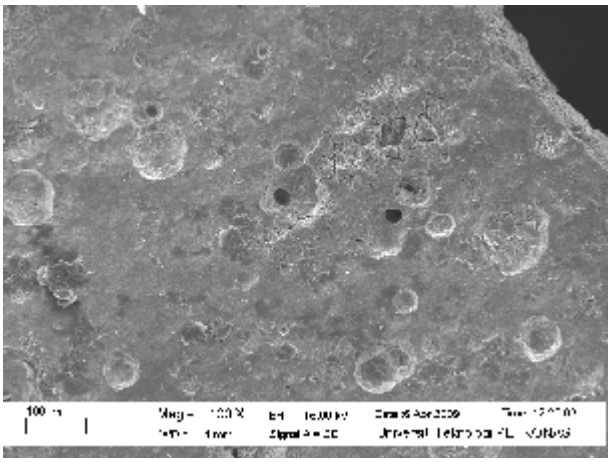


(c)

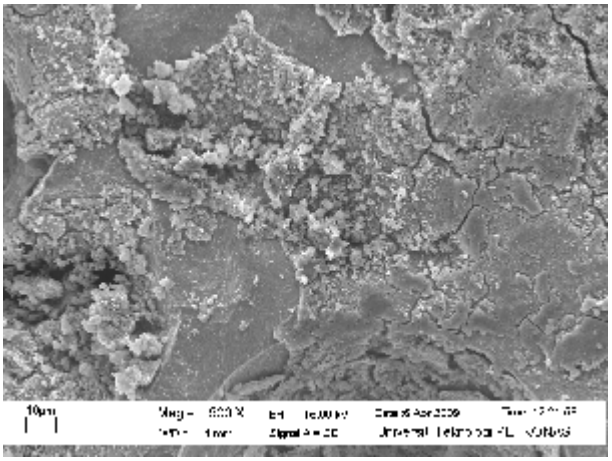
Figure 4.7: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH=5, at pressure of 40 bar and temperature 25℃ (a) 100x (b) 500x (c) 1000x

The SEM images show the corrosion products, $FeCO_3$ film layers formed were porous due to the fact that the experiment was conducted at low temperature (25℃). Some cracks and pitting were identified on the surface due to the high pressure (40 bar) environment used during the test.

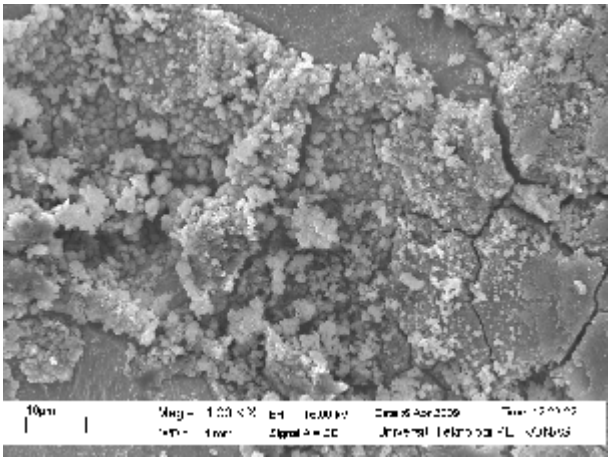
4.4.4 API L-80 Steel after 48 hours immersed in 3% NaCl solutions pH 5, at pressure 60 bar and temperature 25˚C.



(a)



(b)



(c)

Figure 4.8: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH=5, at pressure of 60 bar and temperature 25℃ (a) 100x (b) 500x (c) 1000x

The SEM images show the corrosion products, $FeCO_3$ film layers formed were porous due to the fact that the experiment was conducted at low temperature (25℃). The cracks and pitting occurrence on the surface was higher than previous tests due to the higher pressure (60 bar) environment used during the test.

4.5 Optical Microscopic Test Results

The Optical Microscope Test was conducted to understand the surface condition of the specimens. The OM Tests were conducted on four different L-80 steel specimens:

a. OM image of the initial L-80 steel that not-affected with any electrochemical reaction.
b. OM image of L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 10 bar and temperature of 25°C
c. OM image of L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 40 bar and temperature of 25°C
d. OM image of L 80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 60 bar and temperature of 25°C

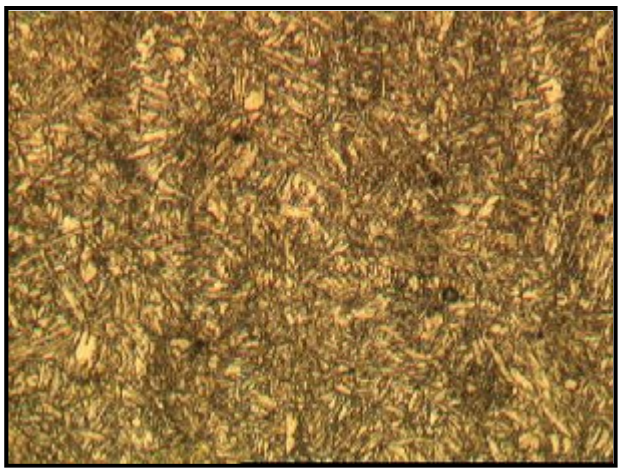


Figure 4.9: OM micrographs of L-80 steel that not-affected with any electrochemical reaction

The OM image above shows the initial surface condition of API L-80 steel specimen before being tested in CO_2 corrosion environment. The surface condition of L-80 steel specimen was smooth and free from any corrosion product.

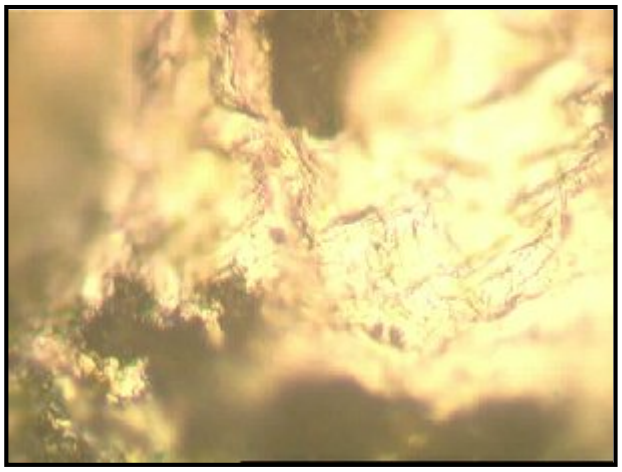


Figure 4.10: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH 5, at pressure of 10 bar and temperature 25℃

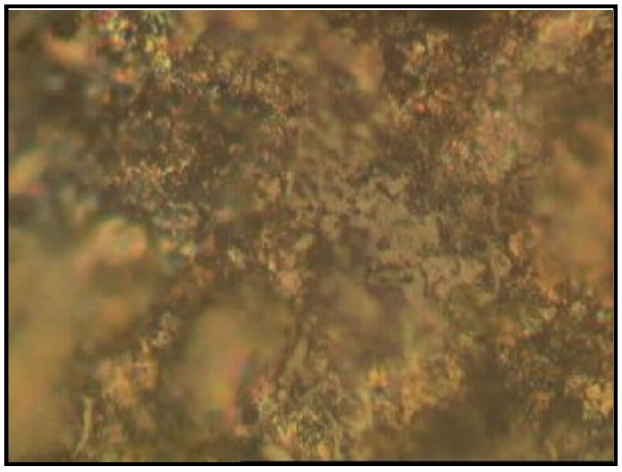


Figure 4.11: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH 5, at pressure of 40 bar and temperature 25℃

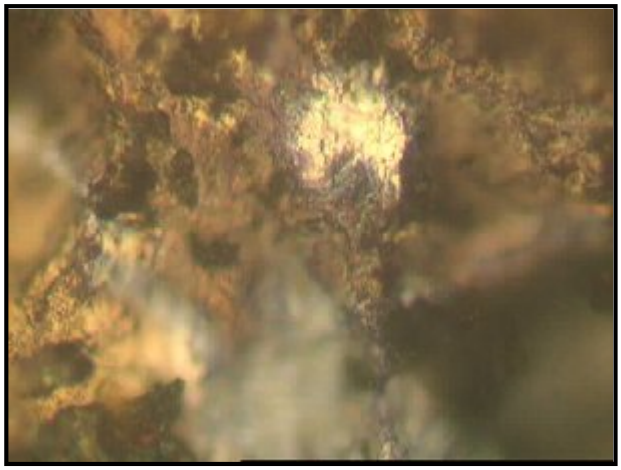


Figure 4.12: L-80 steel specimen at 48 hours immersion in 3% NaCl solution pH 5, at pressure of 60 bar and temperature 25℃

Figure 4.10, 4.11 and 4.12 show that the corrosion product, $FeCO_3$ film layers formed on the surface of the L-80 steel specimen. The surface condition wass rough, due to the existence of the corrosion products.

4.6 Microhardness (Vicker) Tests Results

Hardness covers several properties such as resistance to deformation, resistance to friction and abrasion which is important parameters for tubing failure. Vicker Hardness Test was conducted to compare the L-80 steel's hardness before and after corrosion using Test Load = 50 gf and Dwell Time = 15 seconds. The hardness average (in Hardness Vicker, HV) is shown in Table 4.5 below. 15 tests were conducted on each specimen:

a. L-80 steel that not-affected with any electrochemical reaction.
b. L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 10 bar and temperature of 25°C
c. L-80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 40 bar and temperature of 25°C
d. L 80 steel immersed for 48 hours in CO_2 saturated 3% NaCl solution at pressure 60 bar and temperature of 25°C

Table 4.5: Average Hardness of L-80 Steel Specimens

	Hardness Vicker (HV)			
No. of Test	**Non Corroded L 80 steel**	*** 10 bar**	*** 40 bar**	*** 60 bar**
1	984.4	914.6	907.6	947.9
2	973.4	893.4	933.6	900.4
3	835.4	895.8	833.5	874.0
4	916.2	911.2	904.8	960.5
5	958.6	938.2	921.9	966.4
6	958.6	928.6	915.9	922.6
7	849.1	841.1	917.7	970.4
8	914.4	898.7	829.2	986.9
9	953.7	950.9	941.5	948.7
10	924.4	914.9	919.3	877.4
11	970.4	975.4	955.5	870.5
12	868.9	855.9	977.3	928.1
13	993.6	989.3	965.3	892.9
14	958.6	940.8	938.5	904.6
15	951.8	955.2	932.1	855.6
Average	**934.10**	**920.27**	**919.58**	**920.46**

* L 80 steel immersed for 48 hours in CO2 saturated 3% NaCl solution at temperature of 25°C

4.6.1 Microhardness (Vicker) Test: Discussion

From the test, the L-80 steel that was not affected with any electrochemical reaction yields average hardness = 934.10 HV. It can be seen that the average hardness of the corroded L-80 steel specimens are not much different with the L-80 specimen in the pressure of 10 bar environment yields average hardness = 920.27 HV, the L-80 specimen in the pressure of 40 bar environment yields average hardness = 919.58 HV and the L-80 specimen in the pressure of 60 bar environment yields average hardness = 920.46 HV.

Based on the theory, electrochemical reaction will not affect the hardness of a material. The test was conducted to prove the theory accuracy with the API L-80 steel material in CO_2 corrosion environment.

From the results obtained, the initial average hardness of L-80 steel was 934.10 HV and the average hardness of corroded L-80 steel was in the range of 919.5 to 920.5 HV. The reason of the decreased value of the L-80 steel average hardness was due to the grinding process that was performed on the specimens to acquire flat surface for the microhardness test to be done.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this project, two (2) different tests were performed to measure the CO_2 corrosion rates in API L-80 steel. The following conclusions could be drawn from the study:

a. The main concern of CO_2 corrosion problem in oil producing well was on the production tubing surface. The other well components such as wellhead, casing and packer were not exposed to the CO_2 corrosion environment during the production. API L-80 steel was the material used in the construction of production tubing.
b. From the Weight Loss Method using Autoclave Tests results, it showed that the corrosion rates increased slowly from low to high pressure (10 bar, 40 bar and 60 bar). The corrosion rate increased due to local depletion of HCO_3^- ions which was favoring the cathodic reaction. The highest corrosion rate yields was at 0.4681 mm/yr (environment; 3 wt% NaCl solution, pressure at 60 bar, pH = 5 and at room temperature).
c. The LPR results showed that at low temperatures (25°C, 40°C and 60°C), the corrosion rate increased as the temperature increased because of high solubility of the $FeCO_3$ film layers. However, at temperature of 80°C, for both environments, the $FeCO_3$ film layers might have become more adherent to the steel surface and more protective in nature resulting in a decrease of the corrosion rate. The highest average corrosion rate obtained was 3.9 mm/yr which was considerably high for the tubing application in oil and gas industry.
d. In conclusion for both experiments, the CO_2 corrosion rates in high pressure condition were found in the range of 0.23 mm/yr to 0.47 mm/yr and the CO_2 corrosion rates in high temperature condition were in the range of 1.3 to 3.9 mm/yr. Thus, the CO_2 corrosion rates in high temperature and high pressure condition of oil producing well may varied from 0.23 to 3.9 mm/yr.
e. In order to ensure cost-effective and safe design of production facilities used in the oil and gas industry e.g. oil production tubing well made from L-80

steel, some methods of prevention were identified to be practically used in the field. 1) The usage of adsorption inhibitor such as amine, amide and imidazoline may enhance the formation of $FeCO_3$ protective layer on the surface of production tubing thus, reduce the CO_2 corrosion rates. 2) Due to the high CO_2 corrosion rate yields from the tests using L-80 steel specimens, other material that has more corrosion resistance than L-80 steel may be considered to be used in the construction of production tubing. For example, the addition of 13% of chromium in the L-80 steel may increase the steel's resistance to corrosive environment. It is also recommended to use 3L epoxy layer on the steel surface will act as a coating and provide protective layer against CO_2 corrosion.

5.2 Recommendations

There are several recommendations that can be performed in future to improve the results of the study:

a. In determining the realistic results, comparison should be made between the experimental results and the calculation using CO_2 corrosion prediction models such as Cassandra and Norsok to verify the reliability and consistency of the results obtained from laboratory experiment.
b. Include the pressure and temperature in one experiment to simulate the actual condition of oil producing well using L 80 steel. The values of the temperatures should be increased up to 120°C and the value of pressure should be increased up to 100 bar. This is because under certain conditions, a difference of 5°C and 5 bar can lead to two different corrosion outcomes.
c. It is known that pH has a strong influence on the CO_2 corrosion rates where it involves in the formation of $FeCO_3$ film layers. Higher pH resulted in faster formation of more protective films and therefore, various pH such as pH 6.3 and pH 6.6 should be included in future work.
d. Variation of CO_2 concentration on corrosion rates should be investigated. CO_2 corrosion rate normally is determined by CO_2 partial pressure which is dependent on the system total pressure and CO_2 concentration.

REFERENCES

[1] Kermani, M. B. and Smith, L. M., *CO_2 Corrosion Control in Oil and Gas Production Design Considerations,* Number 23, London, The Institute of Materials, 1997

[2] Dr A K Samant, *Oil and Gas Corporation Technical Paper*, India, 2003

[3] Grigorescu R., *Schlumberger, ROLL Module,* Romania, 2007

[4] Chaoyang Fu., 2001, *Application of grey relational analysis for corrosion failure of oil tubes*, Corrosion Science 2001

[5] G. Ramona, *Baker Hughes, Oilfield Familiarization,* Houston, USA, 2006

[6] Grigorescu R., *Schlumberger, Production Chemistry,* Romania, 2007

[7] ASTM Committee G01, 2004. *Standard Terminology Relating to Corrosion and Corrosion Testing*. G 15 – 04, ASTM International, United States.

[8] Stern, M., *Corrosion 1,* Newnes- Butterworths, 1976

[9] Stern, M., *Corrosion 2: Corrosion Control,* Newnes –Butterworths, 1976 20:35-20:40

[10] Pourbaix, M., *Electrochemical Corrosion,* 1973

[11] Mansfeld, F., J., *Journal of the Electrochemical. Society*, 1973

[12] R. Baboian., *Corosion Test and Standards: Application and Interpretation* (1995), Philadelphia 307-315

[13] Dean, S. W. Jr., *Corrosion Testing: Encyclopedia of Materials Science and Engineering,* M. B. Ed., Permagon Press, 1986

[14] Stern, M. and Weisert, E. D., *Experimental Observations on the Relation between Polarization Resistance and Corrosion Rate, in ASTM Proceedings,* Vol. 59, American Society for Testing and Materials, Philadelphia, 1959, p. 1280

[15] *Corrosion Control in Petroleum Production,* National Association of Corrosion Engineering, 1979, Houston

[16] M. Stern and A.L. Geary, *Electrochemical Polarization*, Journal *of the Electrochemical Society*, Vol. 104, No.1, 1957, p.56

[17] ASTM Committee G01, 2004. *Standard Practice for Laboratory Immersion Corrosion Testing of Metals*. G 31 – 72, ASTM International, United States.

[18] ASTM Committee G01, 2003. *Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements* G 59 – 97, ASTM International, United States.

APPENDICES

Designation: G 1 – 03

Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens[1]

This standard is issued under the fixed designation G 1; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers suggested procedures for preparing bare, solid metal specimens for tests, for removing corrosion products after the test has been completed, and for evaluating the corrosion damage that has occurred. Emphasis is placed on procedures related to the evaluation of corrosion by mass loss and pitting measurements. (**Warning—**In many cases the corrosion product on the reactive metals titanium and zirconium is a hard and tightly bonded oxide that defies removal by chemical or ordinary mechanical means. In many such cases, corrosion rates are established by mass gain rather than mass loss.)

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 1 and 7.2.

2. Referenced Documents

2.1 *ASTM Standards:*

A 262 Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels[2]

D 1193 Specification for Reagent Water[3]

D 1384 Test Method for Corrosion Test for Engine Coolants in Glassware[4]

D 2776 Test Methods for Corrosivity of Water in the Absence of Heat Transfer (Electrical Methods)[5]

G 15 Terminology Relating to Corrosion and Corrosion Testing[6]

G 16 Guide for Applying Statistics to Analysis of Corrosion Data[6]

G 31 Practice for Laboratory Immersion Corrosion Testing of Metals[6]

G 33 Practice for Recording Data from Atmospheric Corrosion Tests of Metallic-Coated Steel Specimens[6]

G 46 Guide for Examination and Evaluation of Pitting Corrosion[6]

G 50 Practice for Conducting Atmospheric Corrosion Tests on Metals[6]

G 78 Guide for Crevice Corrosion Testing of Iron Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments[6]

3. Terminology

3.1 See Terminology G 15 for terms used in this practice.

4. Significance and Use

4.1 The procedures given are designed to remove corrosion products without significant removal of base metal. This allows an accurate determination of the mass loss of the metal or alloy that occurred during exposure to the corrosive environment.

4.2 These procedures, in some cases, may apply to metal coatings. However, possible effects from the substrate must be considered.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type IV of Specification D 1193.

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[1] This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

Current edition approved October 1, 2003. Published October 2003. Originally approved in 1967. Last previous edition approved in 1999 as G 1 – 90 (1999)$^{\epsilon 1}$.

[2] *Annual Book of ASTM Standards*, Vol 01.03.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

[5] *Discontinued*, replaced by Guide G 96. See 1990 *Annual Book of ASTM Standards*, Vol 03.02.

[6] *Annual Book of ASTM Standards*, Vol 03.02.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

6. Methods for Preparing Specimens for Test

6.1 For laboratory corrosion tests that simulate exposure to service environments, a commercial surface, closely resembling the one that would be used in service, will yield the most meaningful results.

6.2 It is desirable to mark specimens used in corrosion tests with a unique designation during preparation. Several techniques may be used depending on the type of specimen and test.

6.2.1 *Stencil or Stamp*—Most metallic specimens may be marked by stenciling, that is, imprinting the designation code into the metal surface using hardened steel stencil stamps hit with a hammer. The resulting imprint will be visible even after substantial corrosion has occurred. However, this procedure introduces localized strained regions and the possibility of superficial iron contamination in the marked area.

6.2.2 Electric engraving by means of a vibratory marking tool may be used when the extent of corrosion damage is known to be small. However, this approach to marking is much more susceptible to having the marks lost as a result of corrosion damage during testing.

6.2.3 Edge notching is especially applicable when extensive corrosion and accumulation of corrosion products is anticipated. Long term atmospheric tests and sea water immersion tests on steel alloys are examples where this approach is applicable. It is necessary to develop a code system when using edge notches.

6.2.4 Drilled holes may also be used to identify specimens when extensive metal loss, accumulation of corrosion products, or heavy scaling is anticipated. Drilled holes may be simpler and less costly than edge notching. A code system must be developed when using drilled holes. Punched holes should not be used as they introduce residual strain.

6.2.5 When it is undesirable to deform the surface of specimens after preparation procedures, for example, when testing coated surfaces, tags may be used for specimen identification. A metal or plastic wire can be used to attach the tag to the specimen and the specimen identification can be stamped on the tag. It is important to ensure that neither the tag nor the wire will corrode or degrade in the test environment. It is also important to be sure that there are no galvanic interactions between the tag, wire, and specimen.

6.3 For more searching tests of either the metal or the environment, standard surface finishes may be preferred. A suitable procedure might be:

6.3.1 Degrease in an organic solvent or hot alkaline cleaner. (See also Practice G 31.)

NOTE 1—Hot alkalies and chlorinated solvents may attack some metals.

NOTE 2—Ultrasonic cleaning may be beneficial in both pre-test and post-test cleaning procedures.

6.3.2 Pickle in an appropriate solution if oxides or tarnish are present. In some cases the chemical cleaners described in Section 6 will suffice.

NOTE 3—Pickling may cause localized corrosion on some materials.

6.3.3 Abrade with a slurry of an appropriate abrasive or with an abrasive paper (see Practices A 262 and Test Method D 1384). The edges as well as the faces of the specimens should be abraded to remove burrs.

6.3.4 Rinse thoroughly, hot air dry, and store in desiccator.

6.4 When specimen preparation changes the metallurgical condition of the metal, other methods should be chosen or the metallurgical condition must be corrected by subsequent treatment. For example, shearing a specimen to size will cold work and may possibly fracture the edges. Edges should be machined.

6.5 The clean, dry specimens should be measured and weighed. Dimensions determined to the third significant figure and mass determined to the fifth significant figure are suggested. When more significant figures are available on the measuring instruments, they should be recorded.

7. Methods for Cleaning After Testing

7.1 Corrosion product removal procedures can be divided into three general categories: mechanical, chemical, and electrolytic.

7.1.1 An ideal procedure should remove only corrosion products and not result in removal of any base metal. To determine the mass loss of the base metal when removing corrosion products, replicate uncorroded control specimens should be cleaned by the same procedure being used on the test specimen. By weighing the control specimen before and after cleaning, the extent of metal loss resulting from cleaning can be utilized to correct the corrosion mass loss.

NOTE 4—It is desirable to scrape samples of corrosion products before using any chemical techniques to remove them. These scrapings can then be subjected to various forms of analyses, including perhaps X-ray diffraction to determine crystal forms as well as chemical analyses to look for specific corrodants, such as chlorides. All of the chemical techniques that are discussed in Section 7 tend to destroy the corrosion products and thereby lose the information contained in these corrosion products. Care may be required so that uncorroded metal is not removed with the corrosion products.

7.1.2 The procedure given in 7.1.1 may not be reliable when heavily corroded specimens are to be cleaned. The application of replicate cleaning procedures to specimens with corroded surfaces will often, even in the absence of corrosion products, result in continuing mass losses. This is because a corroded surface, particularly of a multiphase alloy, is often more susceptible than a freshly machined or polished surface to corrosion by the cleaning procedure. In such cases, the following method of determining the mass loss due to the cleaning procedure is preferred.

7.1.2.1 The cleaning procedure should be repeated on specimens several times. The mass loss should be determined after each cleaning by weighing the specimen.

7.1.2.2 The mass loss should be graphed as a function of the number of equal cleaning cycles as shown in Fig. 1. Two lines will be obtained: AB and BC. The latter will correspond to corrosion of the metal after removal of corrosion products. The mass loss due to corrosion will correspond approximately to point B.

7.1.2.3 To minimize uncertainty associated with corrosion of the metal by the cleaning method, a method should be chosen to provide the lowest slope (near to horizontal) of line BC.

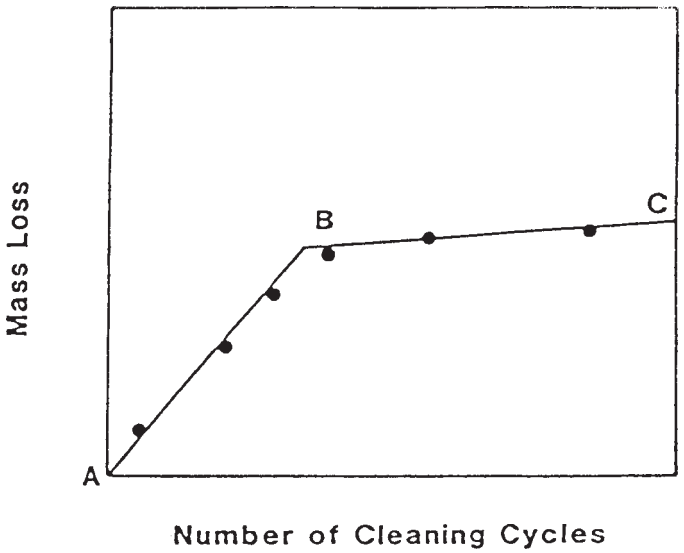

FIG. 1 Mass Loss of Corroded Specimens Resulting from Repetitive Cleaning Cycles

7.1.3 Repeated treatment may be required for complete removal of corrosion products. Removal can often be confirmed by examination with a low power microscope (for example, 7× to 30×). This is particularly useful with pitted surfaces when corrosion products may accumulate in pits. This repeated treatment may also be necessary because of the requirements of 7.1.2.1. Following the final treatment, the specimens should be thoroughly rinsed and immediately dried.

7.1.4 All cleaning solutions shall be prepared with water and reagent grade chemicals.

7.2 Chemical procedures involve immersion of the corrosion test specimen in a specific solution that is designed to remove the corrosion products with minimal dissolution of any base metal. Several procedures are listed in Table A1.1. The choice of chemical procedure to be used is partly a matter of trial and error to establish the most effective method for a specific metal and type of corrosion product scale. (**Warning—**These methods may be hazardous to personnel).

7.2.1 Chemical cleaning is often preceded by light brushing (non metallic bristle) or ultrasonic cleaning of the test specimen to remove loose, bulky corrosion products.

7.2.2 Intermittent removal of specimens from the cleaning solution for light brushing or ultrasonic cleaning can often facilitate the removal of tightly adherent corrosion products.

7.2.3 Chemical cleaning is often followed by light brushing or ultrasonic cleaning in reagent water to remove loose products.

7.3 Electrolytic cleaning can also be utilized for removal of corrosion products. Several useful methods for corrosion test specimens of iron, cast iron, or steel are given in Table A2.1.

7.3.1 Electrolytic cleaning should be preceded by brushing or ultrasonic cleaning of the test specimen to remove loose, bulky corrosion products. Brushing or ultrasonic cleaning should also follow the electrolytic cleaning to remove any loose slime or deposits. This will help to minimize any redeposition of metal from reducible corrosion products that would reduce the apparent mass loss.

7.4 Mechanical procedures can include scraping, scrubbing, brushing, ultrasonic cleaning, mechanical shocking, and impact blasting (for example, grit blasting, water-jet blasting, and so forth). These methods are often utilized to remove heavily encrusted corrosion products. Scrubbing with a nonmetallic bristle brush and a mild abrasive-distilled water slurry can also be used to remove corrosion products.

7.4.1 Vigorous mechanical cleaning may result in the removal of some base metal; therefore, care should be exercised. These should be used only when other methods fail to provide adequate removal of corrosion products. As with other methods, correction for metal loss due to the cleaning method is recommended. The mechanical forces used in cleaning should be held as nearly constant as possible.

8. Assessment of Corrosion Damage

8.1 The initial total surface area of the specimen (making corrections for the areas associated with mounting holes) and the mass lost during the test are determined. The average corrosion rate may then be obtained as follows:

$$\text{Corrosion Rate} = (K \times W)/(A \times T \times D) \quad (1)$$

where:

K = a constant (see 8.1.2),
T = time of exposure in hours,
A = area in cm^2,
W = mass loss in grams, and
D = density in g/cm^3 (see Appendix X1).

8.1.1 Corrosion rates are not necessarily constant with time of exposure. See Practice G 31 for further guidance.

8.1.2 Many different units are used to express corrosion rates. Using the units in 7.1 for *T*, *A*, *W*, and *D*, the corrosion rate can be calculated in a variety of units with the following appropriate value of *K*:

Corrosion Rate Units Desired	Constant (*K*) in Corrosion Rate Equation
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimetres per year (mm/y)	8.76×10^4
micrometres per year (um/y)	8.76×10^7
picometres per second (pm/s)	2.78×10^6
grams per square meter per hour ($g/m^2 \cdot h$)	$1.00 \times 10^4 \times D$
milligrams per square decimeter per day (mdd)	$2.40 \times 10^6 \times D$
micrograms per square meter per second ($\mu g/m^2 \cdot s$)	$2.78 \times 10^6 \times D$

NOTE 5—If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convert a corrosion rate in units *X* to a rate in units *Y*, multiply by K_Y/K_X; for example:

$$15 \text{ mpy} = 15 \times (2.78 \times 10^6)/(3.45 \times 10^6) \text{ pm/s} \quad (2)$$

8.1.3 In the case of sacrificial alloy coatings for which there is preferential corrosion of a component whose density differs from that of the alloy, it is preferable to use the density of the corroded component (instead of the initial alloy density) for calculating average thickness loss rate by use of Eq 1. This is done as follows: (1) cleaning to remove corrosion products only and determine the mass loss of the corroded component; (2) stripping the remaining coating to determine the mass of the uncorroded component; (3) chemical analysis of the stripping solution to determine the composition of the uncorroded

component; (4) performing a mass balance to calculate the composition of the corroded component; (5) using the mass and density of the corroded component to calculate the average thickness loss rate by use of Eq 1. An example of this procedure is given in Appendix X2.

The procedure described above gives an average penetration rate of the coating, but the maximum penetration for a multiphase alloy may be larger when the corroded phase is not uniformly distributed across the surface. In such cases, it is generally considered good practice to obtain a cross section through the corroded surface for microscopic examination. This examination will reveal the extent of selective corrosion of particular phases in the coating, and help in understanding the mechanism of attack.

8.2 Corrosion rates calculated from mass losses can be misleading when deterioration is highly localized, as in pitting or crevice corrosion. If corrosion is in the form of pitting, it may be measured with a depth gage or micrometer calipers with pointed anvils (see Guide G 46). Microscopical methods will determine pit depth by focusing from top to bottom of the pit when it is viewed from above (using a calibrated focusing knob) or by examining a section that has been mounted and metallographically polished. The pitting factor is the ratio of the deepest metal penetration to the average metal penetration (as measured by mass loss).

NOTE 6—See Guide G 46 for guidance in evaluating depths of pitting.
NOTE 7—See Guide G 78 for guidance in evaluating crevice corrosion.

8.3 Other methods of assessing corrosion damage are:

8.3.1 *Appearance*—The degradation of appearance by rusting, tarnishing, or oxidation. (See Practice G 33.)

8.3.2 *Mechanical Properties*—An apparent loss in tensile strength will result if the cross-sectional area of the specimen (measured before exposure to the corrosive environment) is reduced by corrosion. (See Practice G 50.) Loss in tensile strength will result if a compositional change, such as dealloying taking place. Loss in tensile strength and elongation will result from localized attack, such as cracking or intergranular corrosion.

8.3.3 *Electrical Properties*—Loss in electrical conductivity can be measured when metal loss results from uniform corrosion. (See Test Methods D 2776.)

8.3.4 *Microscopical Examination*—Dealloying, exfoliation, cracking, or intergranular attack may be detected by metallographic examination of suitably prepared sections.

9. Report

9.1 The report should include the compositions and sizes of specimens, their metallurgical conditions, surface preparations, and cleaning methods as well as measures of corrosion damage, such as corrosion rates (calculated from mass losses), maximum depths of pitting, or losses in mechanical properties.

10. Precision and Bias

10.1 The factors that can produce errors in mass loss measurement include improper balance calibration and standardization. Generally, modern analytical balances can determine mass values to ±0.2 mg with ease and balances are available that can obtain mass values to ±0.02 mg. In general, mass measurements are not the limiting factor. However, inadequate corrosion product removal or overcleaning will affect precision.

10.2 The determination of specimen area is usually the least precise step in corrosion rate determinations. The precision of calipers and other length measuring devices can vary widely. However, it generally is not necessary to achieve better than ±1 % for area measurements for corrosion rate purposes.

10.3 The exposure time can usually be controlled to better than ±1 % in most laboratory procedures. However, in field exposures, corrosive conditions can vary significantly and the estimation of how long corrosive conditions existed can present significant opportunities for error. Furthermore, corrosion processes are not necessarily linear with time, so that rate values may not be predictive of the future deterioration, but only are indications of the past exposure.

10.4 Regression analysis on results, as are shown in Fig. 1, can be used to obtain specific information on precision. See Guide G 16 for more information on statistical analysis.

10.5 Bias can result from inadequate corrosion product removal or metal removal caused by overcleaning. The use of repetitive cleaning steps, as shown in Fig. 1, can minimize both of these errors.

10.5.1 Corrosion penetration estimations based on mass loss can seriously underestimate the corrosion penetration caused by localized processes, such as pitting, cracking, crevice corrosion, and so forth.

11. Keywords

11.1 cleaning; corrosion product removal; evaluation; mass loss; metals; preparation; specimens

ANNEXES

(Mandatory Information)

A1. CHEMICAL CLEANING PROCEDURES

TABLE A1.1 CHEMICAL CLEANING PROCEDURES FOR REMOVAL OF CORROSION PRODUCTS

Designation	Material	Solution	Time	Temperature	Remarks
C.1.1	Aluminum and Aluminum Alloys	50 mL phosphoric acid (H_3PO_4, sp gr 1.69) 20 g chromium trioxide (CrO_3) Reagent water to make 1000 mL	5 to 10 min	90°C to Boiling	If corrosion product films remain, rinse, then follow with nitric acid procedure (C.1.2).
C.1.2		Nitric acid (HNO_3, sp gr 1.42)	1 to 5 min	20 to 25°C	Remove extraneous deposits and bulky corrosion products to avoid reactions that may result in excessive removal of base metal.
C.2.1	Copper and Copper Alloys	500 mL hydrochloric acid (HCl, sp gr 1.19) Reagent water to make 1000 mL	1 to 3 min	20 to 25°C	Deaeration of solution with purified nitrogen will minimize base metal removal.
C.2.2		4.9 g sodium cyanide (NaCN) Reagent water to make 1000 mL	1 to 3 min	20 to 25°C	Removes copper sulfide corrosion products that may not be removed by hydrochloric acid treatment (C.2.1).
C.2.3		100 mL sulfuric acid (H_2SO_4, sp gr 1.84) Reagent water to make 1000 mL	1 to 3 min	20 to 25°C	Remove bulky corrosion products before treatment to minimize copper redeposition on specimen surface.
C.2.4		120 mL sulfuric acid (H_2SO_4, sp gr 1.84) 30 g sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) Reagent water to make 1000 mL	5 to 10 s	20 to 25°C	Removes redeposited copper resulting from sulfuric acid treatment.
C.2.5		54 mL sulfuric acid (H_2SO_4, sp gr 1.84) Reagent water to make 1000 mL	30 to 60 min	40 to 50°C	Deaerate solution with nitrogen. Brushing of test specimens to remove corrosion products followed by re-immersion for 3 to 4 s is recommended.
C.3.1	Iron and Steel	1000 mL hydrochloric acid (HCl, sp gr 1.19) 20 g antimony trioxide (Sb_2O_3) 50 g stannous chloride ($SnCl_2$)	1 to 25 min	20 to 25°C	Solution should be vigorously stirred or specimen should be brushed. Longer times may be required in certain instances.
C.3.2		50 g sodium hydroxide (NaOH) 200 g granulated zinc or zinc chips Reagent water to make 1000 mL	30 to 40 min	80 to 90°C	Caution should be exercised in the use of any zinc dust since spontaneous ignition upon exposure to air can occur.
C.3.3		200 g sodium hydroxide (NaOH) 20 g granulated zinc or zinc chips Reagent water to make 1000 mL	30 to 40 min	80 to 90°C	Caution should be exercised in the use of any zinc dust since spontaneous ignition upon exposure to air can occur.
C.3.4		200 g diammonium citrate ($(NH_4)_2HC_6H_5O_7$) Reagent water to make 1000 mL	20 min	75 to 90°C	Depending upon the composition of the corrosion product, attack of base metal may occur.
C.3.5		500 mL hydrochloric acid (HCl, sp gr 1.19) 3.5 g hexamethylene tetramine Reagent water to make 1000 mL	10 min	20 to 25°C	Longer times may be required in certain instances.
C.3.6		Molten caustic soda (NaOH) with 1.5–2.0 % sodium hydride (NaH)	1 to 20 min	370°C	For details refer to Technical Information Bulletin SP29-370, "DuPont Sodium Hydride Descaling Process Operating Instructions.''
C.4.1	Lead and Lead Alloys	10 mL acetic acid (CH_3COOH) Reagent water to make 1000 mL	5 min	Boiling	...
C.4.2		50 g ammonium acetate (CH_3COONH_4) Reagent water to make 1000 mL	10 min	60 to 70°C	...
C.4.3		250 g ammonium acetate (CH_3COONH_4) Reagent water to make 1000 mL	5 min	60 to 70°C	...
C.5.1	Magnesium and Magnesium Alloys	150 g chromium trioxide (CrO_3) 10 g silver chromate (Ag_2CrO_4) Reagent water to make 1000 mL	1 min	Boiling	The silver salt is present to precipitate chloride.
C.5.2		200 g chromium trioxide (CrO_3) 10 g silver nitrate ($AgNO_3$) 20 g barium nitrate ($Ba(NO_3)_2$) Reagent water to make 1000 mL	1 min	20 to 25°C	The barium salt is present to precipitate sulfate.
C.6.1	Nickel and Nickel Alloys	150 mL hydrochloric acid (HCl, sp gr 1.19) Reagent water to make 1000 mL	1 to 3 min	20 to 25°C	...
C.6.2		100 mL sulfuric acid (H_2SO_4, sp gr 1.84) Reagent water to make 1000 mL	1 to 3 min	20 to 25°C	...
C.7.1	Stainless Steels	100 mL nitric acid (HNO_3, sp gr 1.42) Reagent water to make 1000 mL	20 min	60°C	...

TABLE A1.1 *Continued*

Designation	Material	Solution	Time	Temperature	Remarks
C.7.2		150 g diammonium citrate ($(NH_4)_2HC_6H_5O_7$) Reagent water to make 1000 mL	10 to 60 min	70°C	...
C.7.3		100 g citric acid ($C_6H_8O_7$) 50 mL sulfuric acid (H_2SO_4, sp gr 1.84) 2 g inhibitor (diorthotolyl thiourea or quinoline ethyliodide or betanaphthol quinoline) Reagent water to make 1000 mL	5 min	60°C	...
C.7.4		200 g sodium hydroxide (NaOH) 30 g potassium permanganate ($KMnO_4$) Reagent water to make 1000 mL *followed by* 100 g diammonium citrate ($(NH_4)_2HC_6H_5O_7$) Reagent water to make 1000 mL	5 min	Boiling	...
C.7.5		100 mL nitric acid (HNO_3, sp gr 1.42) 20 mL hydrofluoric acid (HF, sp gr 1.198–48 %) Reagent water to make 1000 mL	5 to 20 min	20 to 25°C	...
C.7.6		200 g sodium hydroxide (NaOH) 50 g zinc powder Reagent water to make 1000 mL	20 min	Boiling	Caution should be exercised in the use of any zinc dust since spontaneous ignition upon exposure to air can occur.
C.8.1	Tin and Tin Alloys	150 g trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) Reagent water to make 1000 mL	10 min	Boiling	...
C.8.2		50 mL hydrochloric acid (HCl, sp gr 1.19) Reagent water to make 1000 mL	10 min	20°C	...
C.9.1	Zinc and Zinc Alloys	150 mL ammonium hydroxide (NH_4OH, sp gr 0.90) Reagent water to make 1000 mL *followed by* 50 g chromium trioxide (CrO_3) 10 g silver nitrate ($AgNO_3$) Reagent water to make 1000 mL	5 min 15 to 20 s	20 to 25°C Boiling	... The silver nitrate should be dissolved in water and added to the boiling chromic acid to prevent excessive crystallization of silver chromate. The chromic acid must be sulfate free to avoid attack of the zinc base metal.
C.9.2		100 g ammonium chloride (NH_4Cl) Reagent water to make 1000 mL	2 to 5 min	70°C	...
C.9.3		200 g chromium trioxide (CrO_3) Reagent water to make 1000 mL	1 min	80°C	Chloride contamination of the chromic acid from corrosion products formed in salt environments should be avoided to prevent attack of the zinc base metal.
C.9.4		85 mL hydriodic acid (HI, sp gr 1.5) Reagent water to make 1000 mL	15 s	20 to 25°C	Some zinc base metal may be removed. A control specimen (3.1.1) should be employed.
C.9.5		100 g ammonium persulfate ($(NH_4)_2S_2O_8$) Reagent water to make 1000 mL	5 min	20 to 25°C	Particularly recommended for galvanized steel.
C.9.6		100 g ammonium acetate (CH_3COONH_4) Reagent water to make 1000 mL	2 to 5 min	70°C	...

A2. ELECTROLYTIC CLEANING PROCEDURES

TABLE A2.1 ELECTROLYTIC CLEANING PROCEDURES FOR REMOVAL OF CORROSION PRODUCTS

Designation	Material	Solution	Time	Temperature	Remarks
E.1.1	Iron, Cast Iron, Steel	75 g sodium hydroxide (NaOH) 25 g sodium sulfate (Na_2SO_4) 75 g sodium carbonate (Na_2CO_3) Reagent water to make 1000 mL	20 to 40 min	20 to 25°C	Cathodic treatment with 100 to 200 A/m^2 current density. Use carbon, platinum or stainless steel anode.

TABLE A2.1 *Continued*

Designation	Material	Solution	Time	Temperature	Remarks
E.1.2		28 mL sulfuric acid (H_2SO_4, sp gr 1.84) 0.5 g inhibitor (diorthotolyl thiourea or quinoline ethyliodide or betanaphthol quinoline) Reagent water to make 1000 mL	3 min	75°C	Cathodic treatment with 2000 A/m^2 current density. Use carbon, platinum or lead anode.
E.1.3		100 g diammonium citrate ($(NH_4)_2HC_6H_5O_7$) Reagent water to make 1000 mL	5 min	20 to 25°C	Cathodic treatment with 100 A/m^2 current density. Use carbon or platinum anode.
E.2.1	Lead and Lead Alloys	28 mL sulfuric acid (H_2SO_4, sp gr 1.84) 0.5 g inhibitor (diorthotolyl thiourea or quinoline ethyliodide or betanaphthol quinoline) Reagent water to make 1000 mL	3 min	75°C	Cathodic treatment with 2000 A/m^2 current density. Use carbon, platinum or lead anode.
E.3.1	Copper and Copper Alloys	7.5 g potassium chloride (KCl) Reagent water to make 1000 mL	1 to 3	20 to 25°C	Cathodic treatment with 100 A/m^2 current density. Use carbon or platinum anode.
E.4.1	Zinc and Cadmium	50 g dibasic sodium phosphate (Na_2HPO_4) Reagent water to make 1000 mL	5 min	70°C	Cathodic treatment with 110 A/m^2 current density. Specimen must be energized prior to immersion. Use carbon, platinum or stainless steel anode.
E.4.2		100 g sodium hydroxide (NaOH) Reagent water to make 1000 mL	1 to 2 min	20 to 25°C	Cathodic treatment with 100 A/m^2 current density. Specimen must be energized prior to immersion. Use carbon, platinum or stainless steel anode.
E.5.1	General (excluding Aluminum, Magnesium and Tin Alloys)	20 g sodium hydroxide (NaOH) Reagent water to make 1000 mL	5 to 10 min	20 to 25°C	Cathodic treatment with 300 A/m^2 current density. A S31600 stainless steel anode may be used.

APPENDIXES

(Nonmandatory Information)

X1. DENSITIES FOR A VARIETY OF METALS AND ALLOYS

TABLE X1.1 DENSITIES FOR A VARIETY OF METALS AND ALLOYS

NOTE 1—All UNS numbers that include the letter X indicate a series of numbers under one category.
NOTE 2—An asterisk indicates that a UNS number not available.

UNS Number	Alloy	Density g/cm^3
	Aluminum Alloys	
A91100	1100	2.71
A91199	1199	2.70
A92024	2024	2.78
A92219	2219	2.84
A93003	3003	2.73
A93004	3004	2.72
A95005	5005	2.70
A95050	5050	2.69
A95052	5052	2.68
A95083	5083	2.66
A95086	5086	2.66
A95154	5154	2.66
A95357	5357	2.69
A95454	5454	2.69
A95456	5456	2.66
A96061	6061	2.70
*	6062	2.70
A96070	6070	2.71
A96101	6101	2.70
A97075	7075	2.81
A97079	7079	2.75
A97178	7178	2.83
	Stainless Steels	
S20100	Type 201	7.94
S20200	Type 202	7.94
S30200	Type 302	7.94
S30400	Type 304	7.94

TABLE X1.1 *Continued*

UNS Number	Alloy	Density g/cm^3
	Aluminum Alloys	
S30403	Type 304L	7.94
S30900	Type 309	7.98
S31000	Type 310	7.98
S31100	Type 311	7.98
S31600	Type 316	7.98
S31603	Type 316L	7.98
S31700	Type 317	7.98
S32100	Type 321	7.94
S32900	Type 329	7.98
N08330	Type 330	7.98
S34700	Type 347	8.03
S41000	Type 410	7.70
S43000	Type 430	7.72
S44600	Type 446	7.65
S50200	Type 502	7.82
	Other Ferrous Metals	
F1XXXX	Gray cast iron	7.20
GXXXXX–KXXXXX	Carbon steel	7.86
*	Silicon iron	7.00
KXXXXX	Low alloy steels	7.85
	Copper Alloys	
C38600	Copper	8.94
C23000	Red brass 230	8.75
C26000	Cartridge brass 260	8.52
C28000	Muntz metal 280	8.39
*	Admiralty 442	8.52
C44300	Admiralty 443	8.52
C44400	Admiralty 444	8.52
C44500	Admiralty 445	8.52
C68700	Aluminum brass 687	8.33
C22000	Commercial bronze 220	8.80
C60800	Aluminum bronze, 5 % 608	8.16
*	Aluminum bronze, 8 % 612	7.78
*	Composition M	8.45
*	Composition G	8.77
C51000	Phosphor bronze, 5 % 510	8.86
C52400	Phosphor bronze, 10 % 524	8.77
*	85-5-5-5	8.80
C65500	Silicon bronze 655	8.52
C70600	Copper nickel 706	8.94
C71000	Copper nickel 710	8.94
C71500	Copper nickel 715	8.94
C75200	Nickel silver 752	8.75
	Lead	
L53305–53405	Antimonial	10.80
L5XXXX	Chemical	11.33
Nickel Alloys		
N02200	Nickel 200	8.89
N04400	Nickel copper 400	8.84
N06600	Nickel chromium iron alloy 600	8.51
N06625	Nickel chromium molybdenum alloy 625	8.44
N08825	Iron nickel chromium alloy 825	8.14
N08020	Iron nickel chromium alloy 20 Cb-3	8.08
*	Iron nickel chromium cast alloy 20	8.02
N10665	Nickel molybdenum alloy B2	9.2
N10276	Nickel chromium molybdenum alloy C-276	8.8
N06985	Nickel chromium molybdenum alloy G-3	8.3
	Other Metals	
M1XXXX	Magnesium	1.74
R03600	Molybdenum	10.22
P04980	Platinum	21.45
P07016	Silver	10.49
R05200	Tantalum	16.60
L13002	Tin	7.30
R50250	Titanium	4.54
Z13001	Zinc	7.13
R60001	Zirconium	6.53

X2. CALCULATION OF AVERAGE THICKNESS LOSS RATE OF AN ALLOY WHEN THE DENSITY OF THE CORRODING METAL DIFFERS FROM THAT OF THE BULK ALLOY

X2.1 Example

X2.1.1 55% Al-Zn alloy coating on steel sheet exposed for 20.95 years at Point Reyes, CA. (As reported in H.E. Townsend and H.H.Lawson, "Twenty-One Year Results for Metallic-Coated Sheet in the ASTM 1976 Atmospheric Corrosion Tests").[8]

X2.2 Measurements

X2.2.1 Initial aluminum content of coating, C_1, as measured by stripping (Table A1.1, C.3.) and chemical analysis of uncorroded specimens.

$$C_1 = 55.0\%\ \text{Al} \tag{X2.1}$$

X2.2.2 Time of Exposure, T

$$T = 20.95\ \text{years} = 183\,648\ \text{hours} \tag{X2.2}$$

X2.2.3 Specimen Area, A

$$A = 300\ \text{cm}^2 \tag{X2.3}$$

X2.2.4 Initial Mass, W_1

$$W_1 = 79.3586\ \text{g} \tag{X2.4}$$

X2.2.5 Mass after exposure and removal of corrosion products according to Table A1.1, C.9.3, W_2

$$W_2 = 78.7660\ \text{g} \tag{X2.5}$$

X2.2.6 Mass after removal of remaining coating according to Table A1.1, C.3.5, W_3

$$W_3 = 75.0810\ \text{g} \tag{X2.6}$$

X2.2.7 Aluminum content of remaining uncorroded coating by chemical analysis of the stripping solution, C_u

$$C_u = 57.7\%\ \text{Al} \tag{X2.7}$$

X2.3 Calculations

X2.3.1 Mass loss of corroded coating, W

$$W = W_1 - W_2 = 79.3586 - 78.7660 = 0.5926\ \text{g} \tag{X2.8}$$

X2.3.2 Mass of remaining uncorroded coating, W_u

$$W_u = W_2 - W_3 = 78.7660 - 75.0810 = 3.6850\ \text{g} \tag{X2.9}$$

X2.3.3 Total mass of original coating, W_t

$$W_t = W + W_u = 0.5926 + 3.6850 = 4.2776\ \text{g} \tag{X2.10}$$

X2.3.4 Composition of corroded coating, C

$$CW + C_u W_u = C_1 W_t \tag{X2.11}$$

Rearranging gives

$$C = (C_1 W_t - C_u W_u)/W \tag{X2.12}$$

$$C = (55.0 \times 4.2776 - 57.7 \times 3.6850)/0.5926 \tag{X2.13}$$

$$C = 38.2\ \%\ Al \tag{X2.14}$$

X2.3.5 The density, D, of a 38.2 % Al-Zn alloy is 4.32 g/cm^{-3}. In cases where alloy densities are not known, they can be estimated by linear interpolation of the component densities.

X2.3.6 Calculate the average thickness loss rate, L (corrosion rate per Eq 1).

$$L = (K \times W)/(A \times T \times D) \tag{X2.15}$$

where K is given in 8.1.2 as 8.76×10^7

$L = (8.76 \times 10^7 \times 0.5926)/(300 \times 183\,648 \times 4.32)$

$L = 0.218$ micrometres per year

[8] Outdoor Atmospheric Corrosion, STP 1421, H. E. Townsend, Ed., American Society for Testing and MAterials, West Conshohocken, PA, 2002, pp. 284–291.

Designation: G 31 – 72 (Reapproved 2004)

Standard Practice for Laboratory Immersion Corrosion Testing of Metals[1]

This standard is issued under the fixed designation G 31; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice[2] describes accepted procedures for and factors that influence laboratory immersion corrosion tests, particularly mass loss tests. These factors include specimen preparation, apparatus, test conditions, methods of cleaning specimens, evaluation of results, and calculation and reporting of corrosion rates. This practice also emphasizes the importance of recording all pertinent data and provides a checklist for reporting test data. Other ASTM procedures for laboratory corrosion tests are tabulated in the Appendix. (**Warning—**In many cases the corrosion product on the reactive metals titanium and zirconium is a hard and tightly bonded oxide that defies removal by chemical or ordinary mechanical means. In many such cases, corrosion rates are established by mass gain rather than mass loss.)

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [3]

A 262 Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels

E 8 Test Methods for Tension Testing of Metallic Materials

G 1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens

G 4 Guide for Conducting Corrosion Coupon Tests in Field Applications

G 16 Guide for Applying Statistics to Analysis of Corrosion Data

G 46 Guide for Examination and Evaluation of Pitting Corrosion

3. Significance and Use

3.1 Corrosion testing by its very nature precludes complete standardization. This practice, rather than a standardized procedure, is presented as a guide so that some of the pitfalls of such testing may be avoided.

3.2 Experience has shown that all metals and alloys do not respond alike to the many factors that affect corrosion and that "accelerated" corrosion tests give indicative results only, or may even be entirely misleading. It is impractical to propose an inflexible standard laboratory corrosion testing procedure for general use, except for material qualification tests where standardization is obviously required.

3.3 In designing any corrosion test, consideration must be given to the various factors discussed in this practice, because these factors have been found to affect greatly the results obtained.

4. Interferences

4.1 The methods and procedures described herein represent the best current practices for conducting laboratory corrosion tests as developed by corrosion specialists in the process industries. For proper interpretation of the results obtained, the specific influence of certain variables must be considered. These include:

4.1.1 Metal specimens immersed in a specific hot liquid may not corrode at the same rate or in the same manner as in equipment where the metal acts as a heat transfer medium in heating or cooling the liquid. If the influence of heat transfer effects is specifically of interest, specialized procedures (in which the corrosion specimen serves as a heat transfer agent) must be employed (**1**).[4]

4.1.2 In laboratory tests, the velocity of the environment relative to the specimens will normally be determined by convection currents or the effects induced by aeration or boiling or both. If the specific effects of high velocity are to be studied, special techniques must be employed to transfer the

[1] This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

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[2] This practice is based upon NACE Standard TM-01-69, "Test Method-Laboratory Corrosion Testing of Metals for the Process Industries," with modifications to relate more directly to Practices G 1 and G 31 and Guide G 4.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The boldface numbers in parentheses refer to the list of references at the end of this practice.

environment through tubular specimens or to move it rapidly past the plane face of a corrosion coupon (**2**). Alternatively, the coupon may be rotated through the environment, although it is then difficult to evaluate the velocity quantitatively because of the stirring effects incurred.

4.1.3 The behavior of certain metals and alloys may be profoundly influenced by the presence of dissolved oxygen. If this is a factor to be considered in a specific test, the solution should be completely aerated or deaerated in accordance with 8.7.

4.1.4 In some cases, the rate of corrosion may be governed by other minor constituents in the solution, in which case they will have to be continually or intermittently replenished by changing the solution in the test.

4.1.5 Corrosion products may have undesirable effects on a chemical product. The amount of possible contamination can be estimated from the loss in mass of the specimen, with proper application of the expected relationships among (*1*) the area of corroding surface, (*2*) the mass of the chemical product handled, and (*3*) the duration of contact of a unit of mass of the chemical product with the corroding surface.

4.1.6 Corrosion products from the coupon may influence the corrosion rate of the metal itself or of different metals exposed at the same time. For example, the accumulation of cupric ions in the testing of copper alloys in intermediate strengths of sulfuric acid will accelerate the corrosion of copper alloys, as compared to the rates that would be obtained if the corrosion products were continually removed. Cupric ions may also exhibit a passivating effect upon stainless steel coupons exposed at the same time. In practice, only alloys of the same general type should be exposed in the testing apparatus.

4.1.7 Coupon corrosion testing is predominantly designed to investigate general corrosion. There are a number of other special types of phenomena of which one must be aware in the design and interpretation of corrosion tests.

4.1.7.1 Galvanic corrosion may be investigated by special devices which couple one coupon to another in electrical contact. The behavior of the specimens in this galvanic couple are compared with that of insulated specimens exposed on the same holder and the galvanic effects noted. It should be observed, however, that galvanic corrosion can be greatly affected by the area ratios of the respective metals, the distance between the metals and the resistivity of the electrolyte. The coupling of corrosion coupons then yields only qualitative results, as a particular coupon reflects only the relationship between these two metals at the particular area ratio involved.

4.1.7.2 Crevice corrosion or concentration cell corrosion may occur where the metal surface is partially blocked from the corroding liquid as under a spacer or supporting hook. It is necessary to evaluate this localized corrosion separately from the overall mass loss.

4.1.7.3 Selective corrosion at the grain boundaries (for example, intergranular corrosion of sensitized austenitic stainless steels) will not be readily observable in mass loss measurements unless the attack is severe enough to cause grain dropping, and often requires microscopic examination of the coupons after exposure.

4.1.7.4 Dealloying or “parting” corrosion is a condition in which one constituent is selectively removed from an alloy, as in the dezincification of brass or the graphitization of cast iron. Close attention and a more sophisticated evaluation than a simple mass loss measurement are required to detect this phenomenon.

4.1.7.5 Certain metals and alloys are subject to a highly localized type of attack called pitting corrosion. This cannot be evaluated by mass loss alone. The reporting of nonuniform corrosion is discussed below. It should be appreciated that pitting is a statistical phenomenon and that the incidence of pitting may be directly related to the area of metal exposed. For example, a small coupon is not as prone to exhibit pitting as a large one and it is possible to miss the phenomenon altogether in the corrosion testing of certain alloys, such as the AISI Type 300 series stainless steels in chloride contaminated environments.

4.1.7.6 All metals and alloys are subject to stress-corrosion cracking under some circumstances. This cracking occurs under conditions of applied or residual tensile stress, and it may or may not be visible to the unaided eye or upon casual inspection. A metallographic examination may confirm the presence of stress-corrosion cracking. It is imperative to note that this usually occurs with no significant loss in mass of the test coupon, although certain refractory metals are an exception to these observations. Generally, if cracking is observed on the coupon, it can be taken as positive indication of susceptibility, whereas failure to effect this phenomenon simply means that it did not occur under the duration and specific conditions of the test. Separate and special techniques are employed for the specific evaluation of the susceptibility of metals and alloys to stress corrosion cracking (see Ref. **(3)**).

5. Apparatus

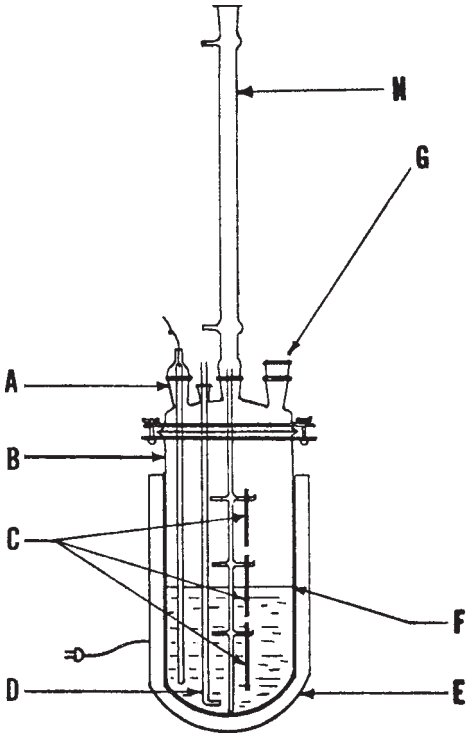
5.1 A versatile and convenient apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5000 mL), a reflux condenser with atmospheric seal, a sparger for controlling atmosphere or aeration, a thermowell and temperature-regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. If agitation is required, the apparatus can be modified to accept a suitable stirring mechanism, such as a magnetic stirrer. A typical resin flask setup for this type test is shown in Fig. 1.

5.2 The suggested components can be modified, simplified, or made more sophisticated to fit the needs of a particular investigation. The suggested apparatus is basic and the apparatus is limited only by the judgment and ingenuity of the investigator.

5.2.1 A glass reaction kettle can be used where the configuration and size of the specimen will permit entry through the narrow kettle neck (for example, 45/50 ground-glass joint). For solutions corrosive to glass, suitable metallic or plastic kettles may be employed.

5.2.2 In some cases a wide-mouth jar with a suitable closure is sufficient when simple immersion tests at ambient temperatures are to be investigated.

5.2.3 Open-beaker tests should not be used because of evaporation and contamination.



NOTE 1—The flask can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of top to flask is such that more sophisticated apparatus can be added as required by the specific test being conducted. *A* = thermowell, *B* = resin flask, *C* = specimens hung on supporting device, *D* = air inlet, *E* = heating mantle, *F* = liquid interface, *G* = opening in flask for additional apparatus that may be required, and *H* = reflux condenser.

FIG. 1 Typical Resin Flask

5.2.4 In more complex tests, provisions might be needed for continuous flow or replenishment of the corrosive liquid, while simultaneously maintaining a controlled atmosphere.

6. Sampling

6.1 The bulk sampling of products is outside the scope of this practice.

7. Test Specimen

7.1 In laboratory tests, uniform corrosion rates of duplicate specimens are usually within ±10 % under the same test conditions. Occasional exceptions, in which a large difference is observed, can occur under conditions of borderline passivity of metals or alloys that depend on a passive film for their resistance to corrosion. Therefore, at least duplicate specimens should normally be exposed in each test.

7.2 If the effects of corrosion are to be determined by changes in mechanical properties, untested duplicate specimens should be preserved in a noncorrosive environment at the same temperature as the test environment for comparison with the corroded specimens. The mechanical property commonly used for comparison is the tensile strength. Measurement of percent elongation is a useful index of embrittlement. The procedures for determining these values are shown in detail in Test Methods E 8.

7.3 The size and shape of specimens will vary with the purpose of the test, nature of the materials, and apparatus used. A large surface-to-mass ratio and a small ratio of edge area to total area are desirable. These ratios can be achieved through the use of square or circular specimens of minimum thickness. Masking may also be used to achieve the desired area ratios but may cause crevice corrosion problems. Circular specimens should preferably be cut from sheet and not bar stock, to minimize the exposed end grain. Special coupons (for example, sections of welded tubing) may be employed for specific purposes.

7.3.1 A circular specimen of about 38-mm (1.5-in.) diameter is a convenient shape for laboratory corrosion tests. With a thickness of approximately 3 mm (0.125-in.) and an 8-mm (5⁄16-in.) or 11-mm (7⁄16-in.) diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = \pi/2(D^2 - d^2) + t\pi D + t\pi d \quad (1)$$

where:

t = thickness,
D = diameter of the specimen, and
d = diameter of the mounting hole.

7.3.1.1 If the hole is completely covered by the mounting support, the last term ($t\pi d$) in the equation is omitted.

7.3.2 Strip coupons 50 by 25 by 1.6 or 3 mm (2 by 1 by 1⁄16 or 1⁄8 in.) may be preferred as corrosion specimens, particularly if interface or liquid line effects are to be studied by the laboratory tests (see Fig. 1), but the evaluation of such specific effects are beyond the scope of this practice.

7.3.3 All specimens should be measured carefully to permit accurate calculation of the exposed areas. A geometric area calculation accurate to ±1 % is usually adequate.

7.4 More uniform results may be expected if a substantial layer of metal is removed from the specimens to eliminate variations in condition of the original metallic surface. This can be done by chemical treatment (pickling), electrolytic removal, or by grinding with a coarse abrasive paper or cloth such as No. 50, using care not to work harden the surface (see section 5.7). At least 0.0025 mm (0.0001 in.) or 0.0155 to 0.0233 mg/mm^2 (10 to 15 mg/in.^{2}) should be removed. (If clad alloy specimens are to be used, special attention must be given to ensure that excessive metal is not removed.) After final preparation of the specimen surface, the specimens should be stored in a desiccator until exposure, if they are not used immediately. In special cases (for example, for aluminum and certain copper alloys), a minimum of 24 h storage in a desiccator is recommended. The choice of a specific treatment must be considered on the basis of the alloy to be tested and the reasons for testing. A commercial surface may sometimes yield the most significant results. Too much surface preparation may remove segregated elements, surface contamination, and so forth, and therefore not be representative.

7.5 Exposure of sheared edges should be avoided unless the purpose of the test is to study effects of the shearing operation. It may be desirable to test a surface representative of the material and metallurgical conditions used in practice.

7.6 The specimen can be stamped with an appropriate identifying mark. If metallic contamination of the stamped area may influence the corrosion behavior, chemical cleaning must be employed to remove any traces of foreign particles from the surface of the coupon (for example, by immersion of stainless steel coupons in dilute nitric acid following stamping with steel dies).

7.6.1 The stamp, besides identifying the specimen, introduces stresses and cold work in the specimen that could be responsible for localized corrosion or stress-corrosion cracking, or both.

7.6.2 Stress-corrosion cracking at the identifying mark is a positive indication of susceptibility to such corrosion. However, the absence of cracking should not be interpreted as indicating resistance (see 4.1.7.6).

7.7 Final surface treatment of the specimens should include finishing with No. 120 abrasive paper or cloth or the equivalent, unless the surface is to be used in the mill finished condition. This resurfacing may cause some surface work hardening, to an extent which will be determined by the vigor of the surfacing operation, but is not ordinarily significant. The surface finish to be encountered in service may be more appropriate for some testing.

7.7.1 Coupons of different alloy compositions should never be ground on the same cloth.

7.7.2 Wet grinding should be used on alloys which work harden quickly, such as the austenitic stainless steels.

7.8 The specimens should be finally degreased by scrubbing with bleach-free scouring powder, followed by thorough rinsing in water and in a suitable solvent (such as acetone, methanol, or a mixture of 50 % methanol and 50 % ether), and air dried. For relatively soft metals (such as aluminum, magnesium, and copper), scrubbing with abrasive powder is not always needed and can mar the surface of the specimen. Proper ultrasonic procedures are an acceptable alternate. The use of towels for drying may introduce an error through contamination of the specimens with grease or lint.

7.9 The dried specimens should be weighed on an analytical balance to an accuracy of at least ±0.5 mg. If cleaning deposits (for example, scouring powder) remain or lack of complete dryness is suspected, then recleaning and drying is performed until a constant mass is attained.

7.10 The method of specimen preparation should be described when reporting test results, to facilitate interpretation of data by other persons.

7.11 The use of welded specimens is sometimes desirable, because some welds may be cathodic or anodic to the parent metal and may affect the corrosion rate.

7.11.1 The heat-affected zone is also of importance but should be studied separately, because welds on coupons do not faithfully reproduce heat input or size effects of full-size weldments.

7.11.2 Corrosion of a welded coupon is best reported by description and thickness measurements rather than a millimetre per year (mils per year) rate, because the attack is normally localized and not representative of the entire surface.

7.11.3 A complete discussion of corrosion testing of welded coupons or the effect of heat treatment on the corrosion resistance of a metal is not within the scope of this practice.

8. Test Conditions

8.1 Selection of the conditions for a laboratory corrosion test will be determined by the purpose of the test.

8.1.1 If the test is to be a guide for the selection of a material for a particular purpose, the limits of the controlling factors in service must be determined. These factors include oxygen concentration, temperature, rate of flow, pH value, composition, and other important characteristics of the solution.

8.2 An effort should be made to duplicate all pertinent service conditions in the corrosion test.

8.3 It is important that test conditions be controlled throughout the test in order to ensure reproducible results.

8.4 The spread in corrosion rate values for duplicate specimens in a given test probably should not exceed ±10 % of the average when the attack is uniform.

8.5 *Composition of Solution*:

8.5.1 Test solutions should be prepared accurately from chemicals conforming to the Specifications of the Committee on Analytical Reagents of the American Chemical Society[5] and distilled water, except in those cases where naturally occurring solutions or those taken directly from some plant process are used.

8.5.2 The composition of the test solutions should be controlled to the fullest extent possible and should be described as completely and as accurately as possible when the results are reported.

8.5.2.1 Minor constituents should not be overlooked because they often affect corrosion rates.

8.5.2.2 Chemical content should be reported as percentage by weight of the solutions. Molarity and normality are also helpful in defining the concentration of chemicals in some test solutions.

8.5.3 If problems are suspected, the composition of the test solutions should be checked by analysis at the end of the test to determine the extent of change in composition, such as might result from evaporation or depletion.

8.5.4 Evaporation losses may be controlled by a constant level device or by frequent addition of appropriate solution to maintain the original volume within ±1 %. Preferably, the use of a reflux condenser ordinarily precludes the necessity of adding to the original kettle charge.

8.5.5 In some cases, composition of the test solution may change as a result of catalytic decomposition or by reaction with the test coupons. These changes should be determined if possible. Where required, the exhausted constituents should be added or a fresh solution provided during the course of the test.

8.5.6 When possible, only one type of metal should be exposed in a given test (see 4.1.6).

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.6 *Temperature of Solution*:

8.6.1 Temperature of the corroding solution should be controlled within ±1°C (±1.8°F) and must be stated in the report of test results.

8.6.2 If no specific temperature, such as boiling point, is required or if a temperature range is to be investigated, the selected temperatures used in the test, and their respective duration, must be reported.

8.6.3 For tests at ambient temperature, the tests should be conducted at the highest temperature anticipated for stagnant storage in summer months. This temperature may be as high as from 40 to 45°C (104 to 113°F) in some areas. The variation in temperature should be reported also (for example, 40 ± 2°C).

8.7 *Aeration of Solution*:

8.7.1 Unless specified, the solution should not be aerated. Most tests related to process equipment should be run with the natural atmosphere inherent in the process, such as the vapors of the boiling liquid.

8.7.2 If aeration is employed, the specimen should not be located in the direct air stream from the sparger. Extraneous effects can be encountered if the air stream impinges on the specimens.

8.7.3 If exclusion of dissolved oxygen is necessary, specific techniques are required, such as prior heating of the solution and sparging with an inert gas (usually nitrogen). A liquid atmospheric seal is required on the test vessel to prevent further contamination.

8.7.4 If oxygen saturation of the test solution is desired, this can best be achieved by sparging with oxygen. For other degrees of aeration, the solution should be sparaged with air or synthetic mixtures of air or oxygen with an inert gas. Oxygen saturation is a function of the partial pressure of oxygen in the gas.

8.8 *Solution Velocity*:

8.8.1 The effect of velocity is not usually determined in normal laboratory tests, although specific tests have been designed for this purpose.

8.8.2 Tests at the boiling point should be conducted with the minimum possible heat input, and boiling chips should be used to avoid excessive turbulence and bubble impingement.

8.8.3 In tests below the boiling point, thermal convection generally is the only source of liquid velocity.

8.8.4 In test solutions with high viscosity, supplemental controlled stirring with a magnetic stirrer is recommended.

8.9 *Volume of Test Solution*:

8.9.1 The volume of the test solution should be large enough to avoid any appreciable change in its corrosivity during the test, either through exhaustion of corrosive constituents or by accumulation of corrosion products that might affect further corrosion.

8.9.2 Two examples of a minimum "solution volume-to-specimen area" ratio are 0.20 mL/mm^2 (125 mL/in.^{2}) of specimen surface (Practice A 262), and 0.40 mL/mm ^{2} (250 mL/in.^{2}).

8.9.3 When the test objective is to determine the effect of a metal or alloy on the characteristics of the test solution (for example, to determine the effects of metals on dyes), it is desirable to reproduce the ratio of solution volume to exposed metal surface that exists in practice. The actual time of contact of the metal with the solution must also be taken into account. Any necessary distortion of the test conditions must be considered when interpreting the results.

8.10 *Method of Supporting Specimens*:

8.10.1 The supporting device and container should not be affected by or cause contamination of the test solution.

8.10.2 The method of supporting specimens will vary with the apparatus used for conducting the test, but should be designed to insulate the specimens from each other physically and electrically and to insulate the specimens from any metallic container or supporting device used within the apparatus.

8.10.3 Shape and form of the specimen support should assure free contact of the specimen with the corroding solution, the liquid line, or the vapor phase as shown in Fig. 1. If clad alloys are exposed, special procedures will be required to ensure that only the cladding is exposed, unless the purpose is to test the ability of the cladding to protect cut edges in the test solution.

8.10.4 Some common supports are glass or ceramic rods, glass saddles, glass hooks, fluorocarbon plastic strings, and various insulated or coated metallic supports.

8.11 *Duration of Test*:

8.11.1 Although duration of any test will be determined by the nature and purpose of the test, an excellent procedure for evaluating the effect of time on corrosion of the metal and also on the corrosiveness of the environment in laboratory tests has been presented by Wachter and Treseder **(4).** This technique is called the "planned interval test," and the procedure and evaluation of results are given in Table 1. Other procedures that require the removal of solid corrosion products between exposure periods will not measure accurately the normal changes of corrosion with time.

8.11.2 Materials that experience severe corrosion generally do not ordinarily need lengthy tests to obtain accurate corrosion rates. However, there are cases where this assumption is not valid. For example, lead exposed to sulfuric acid corrodes at an extremely high rate at first, while building a protective film; then the rates decrease considerably so that further corrosion is negligible. The phenomenon of forming a protective film is observed with many corrosion-resistant materials. Therefore, short tests on such materials would indicate a high corrosion rate and be completely misleading.

8.11.3 Short-time tests also can give misleading results on alloys that form passive films, such as stainless steels. With borderline conditions, a prolonged test may be needed to permit breakdown of the passive film and subsequent more rapid attack. Consequently, tests run for long periods are considerably more realistic than those conducted for short durations. This statement must be qualified by stating that corrosion should not proceed to the point where the original specimen size or the exposed area is drastically reduced or where the metal is perforated.

8.11.4 If anticipated corrosion rates are moderate or low, the following equation gives the suggested test duration:

$$\text{Hours} = 2000/(\text{corrosion rate in mpy}) \quad (2)$$

TABLE 1 Planned Interval Corrosion Test

(Reprinted by permission from Chemical Engineering Progress, June 1947)

Identical specimens all placed in the same corrosive fluid. Imposed conditions of the test kept constant for entire time $t + 1$. Letters, A_1, A_t, A_{t+1}, B, represent corrosion damage experienced by each test specimen. A_2 is calculated by subtracting A_t from A_{t+1}.

Occurrences During Corrosion Test		Criteria
Liquid corrosiveness	unchanged	$A_1 = B$
	decreased	$B < A_1$
	increased	$A_1 < B$
Metal corrodibility	unchanged	$A_2 = B$
	decreased	$A_2 < B$
	increased	$B < A_2$

Combinations of Situations		
Liquid corrosiveness	Metal corrodibility	Criteria
1. unchanged	unchanged	$A_1 = A_2 = B$
2. unchanged	decreased	$A_2 < A_1 = B$
3. unchanged	increased	$A_1 = B < A_2$
4. decreased	unchanged	$A_2 = B < A_1$
5. decreased	decreased	$A_2 < B < A_1$
6. decreased	increased	$A_1 > B < A_2$
7. increased	unchanged	$A_1 < A_2 = B$
8. increased	decreased	$A_1 < B > A_2$
9. increased	increased	$A_1 < B < A_2$

Example; Conditions: Duplicate strips of low-carbon steel, each 19 by 76 mm (¾ by 3 in.), immersed in 200 mL of 10 % $AlCl_3$-90 % $SbCl_3$ mixture through which dried HCl gas was slowly bubbled at atmospheric pressure. Temperature 90°C.

	Interval, days	Mass Loss, mg	Penetration, mm (mils)	Apparent Corrosion Rate, mm/y (mpy)
A_1	0–1	1080	.043 (1.69)	15.7 (620)
A_t	0–3	1430	.057 (2.24)	6.9 (270)
A_{t+1}	0–4	1460	.058 (2.29)	5.3 (210)
B	3–4	70	.003 (0.11)	1.0 (40)
A_2	calc. 3–4	30	.001 (0.05)	0.5 (18)

Example: $A_2 < B < A_1$

.001 < .003 < .043 (0.05 < 0.11 < 1.69)

Therefore, liquid markedly decreased in corrosiveness during test, and formation of partially protective scale on the steel was indicated.

where mpy = mils per year (see 11.2.1 and Note 1 for conversion to other units).

8.11.4.1 *Example*—Where the corrosion rate is 0.25 mm/y (10 mpy), the test should run for at least 200 h.

8.11.4.2 This method of estimating test duration is useful only as an aid in deciding, after a test has been made, whether or not it is desirable to repeat the test for a longer period. The most common testing periods are 48 to 168 h (2 to 7 days).

8.11.5 In some cases, it may be necessary to know the degree of contamination caused by the products of corrosion. This can be accomplished by analysis of the solution after corrosion has occurred. The corrosion rate can be calculated from the concentration of the matrix metal found in the solution and it can be compared to that determined from the mass loss of the specimens. However, some of the corrosion products usually adhere to the specimen as a scale and the corrosion rate calculated from the metal content in the solution is not always correct.

8.12 The design of corrosion testing programs is further discussed in Guide G 16.

9. Methods of Cleaning Specimens after Test

9.1 Before specimens are cleaned, their appearance should be observed and recorded. Location of deposits, variations in types of deposits, or variations in corrosion products are extremely important in evaluating localized corrosion, such as pitting and concentration cell attack.

9.2 Cleaning specimens after the test is a vital step in the corrosion test procedure and if not done properly, can cause misleading results.

9.2.1 Generally, the cleaning procedure should remove all corrosion products from specimens with a minimum removal of sound metal.

9.2.2 Set rules cannot be applied to specimen cleaning, because procedures will vary, depending on the type of metal being cleaned and on the degree of adherence of corrosion products.

9.3 Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

9.3.1 Mechanical cleaning includes scrubbing, scraping, brushing, mechanical shocking, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used principally as a supplement to remove heavily encrusted corrosion products before scrubbing. Care should be used to avoid the removal of sound metal.

9.3.2 Chemical cleaning implies the removal of material from the surface of the specimen by dissolution in an appropriate chemical solution. Solvents such as acetone, carbon tetrachloride, and alcohol are used to remove oil, grease, or resin and are usually applied prior to other methods of cleaning. Chemicals are chosen for application to a specific material. Methods for chemical cleaning after testing of specific metals and alloys are described in Practice G 1.

9.3.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. A method of electrolytic cleaning is described in Practice G 1.

9.3.3.1 Precautions must be taken to ensure good electrical contact with the specimen, to avoid contamination of the solution with easily reducible metal ions, and to ensure that inhibitor decomposition has not occurred.

9.4 Whatever treatment is used to clean specimens after a corrosion test, its effect in removing metal should be determined and the mass loss should be corrected accordingly. A "blank" specimen should be weighed before and after exposure to the cleaning procedure to establish this mass loss (see also Practice G 1). Careful observation is needed to ensure that pitting does not occur during cleaning.

9.4.1 Following removal of all scale, the specimen should be treated as discussed in 5.8.

9.4.2 The description of the cleaning method should be included with the data reported.

10. Interpretation of Results

10.1 After corroded specimens have been cleaned, they should be reweighed with an accuracy corresponding to that of the original weighing. The mass loss during the test period can be used as the principal measure of corrosion.

10.2 After the specimens have been reweighed, they should be examined carefully for the presence of any pits. If there are any pits, the average and maximum depths of pits are determined with a pit gage or a calibrated microscope which can be focused first on the edges and then on the bottoms of the pits. The degree of lateral spreading of pits may also be noted.

10.2.1 Pit depths should be reported in millimetres or thousandths of an inch for the test period and not interpolated or extrapolated to millimetres per year, thousandths of an inch per year, or any other arbitrary period because rarely, if ever, is the rate of initiation or propagation of pits uniform.

10.2.2 The size, shape, and distribution of pits should be noted. A distinction should be made between those occurring underneath the supporting devices (concentration cells) and those on the surfaces that were freely exposed to the test solution (see Guide G 46).

10.3 If the material being tested is suspected of being subject to dealloying forms of corrosion such as dezincification or to intergranular attack, a cross section of the specimen should be microscopically examined for evidence of such attack.

10.4 The specimen may be subjected to simple bending tests to determine whether any embrittlement attack has occurred.

10.5 It may be desirable to make quantitative mechanical tests, comparing the exposed specimens with uncorroded specimens reserved for the purpose, as described in 7.2.

11. Calculating Corrosion Rates

11.1 Calculating corrosion rates requires several pieces of information and several assumptions:

11.1.1 The use of corrosion rates implies that all mass loss has been due to general corrosion and not to localized corrosion, such as pitting or intergranular corrosion of sensitized areas on welded coupons. Localized corrosion is reported separately.

11.1.2 The use of corrosion rates also implies that the material has not been internally attacked as by dezincification or intergranular corrosion.

11.1.3 Internal attack can be expressed as a corrosion rate if desired. However, the calculations must not be based on mass loss (except in qualification tests such as Practices A 262), which is usually small but on microsections which show depth of attack.

11.2 Assuming that localized or internal corrosion is not present or is recorded separately in the report, the average corrosion rate can be calculated by the following equation:

$$\text{Corrosion rate} = (K \times W)/(A \times T \times D) \quad (3)$$

where:

- K = a constant (see below)
- T = time of exposure in hours to the nearest 0.01 h,
- A = area in cm^2 to the nearest 0.01 cm^2,
- W = mass loss in g, to nearest 1 mg (corrected for any loss during cleaning (see 9.4)), and
- D = density in g/cm^3, (see Appendix X1 of Practice G 1).

11.2.1 Many different units are used to express corrosion rates. Using the above units for T, A, W, and D, the corrosion rate can be calculated in a variety of units with the following appropriate value of K:

Corrosion Rate Units Desired	Constant (K) in Corrosion Rate Equation
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimetres per year (mm/y)	8.76×10^4
micrometres per year (μm/y)	8.76×10^7
picometres per second (pm/s)	2.78×10^6
grams per square metre per hour ($g/m^2 \cdot h$)	$1.00 \times 10^4 \times D^A$
milligrams per square decimetre per day (mdd)	$2.40 \times 10^6 \times D^A$
micrograms per square metre per second ($\mu g/m^2 \cdot s$)	$2.78 \times 10^6 \times D^A$

[A] Density is not needed to calculate the corrosion rate in these units. The density in the constant K cancels out the density in the corrosion rate equation.

NOTE 1—If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convert a corrosion rate in units X to a rate of units Y, multiply by K_Y/K_X for example:

$$15 \text{ mpy} = 15 \times [(2.78 \times 10^6)/((3.45 \times 10^6)]\text{pm/s}$$

$$= 12.1 \text{ pm/s} \quad (4)$$

12. Report

12.1 The importance of reporting all data as completely as possible cannot be overemphasized.

12.2 Expansion of the testing program in the future or correlating the results with tests of other investigators will be possible only if all pertinent information is properly recorded.

12.3 The following checklist is a recommended guide for reporting all important information and data.

12.3.1 Corrosive media and concentration (any changes during test).

12.3.2 Volume of test solution.

12.3.3 Temperature (maximum, minimum, average).

12.3.4 Aeration (describe conditions or technique).

12.3.5 Agitation (describe conditions or technique).

12.3.6 Type of apparatus used for test.

12.3.7 Duration of each test.

12.3.8 Chemical composition or trade name of metals tested.

12.3.9 Form and metallurgical conditions of specimens.

12.3.10 Exact size, shape, and area of specimens.

12.3.11 Treatment used to prepare specimens for test.

12.3.12 Number of specimens of each material tested, and whether specimens were tested separately or which specimens tested in the same container.

12.3.13 Method used to clean specimens after exposure and the extent of any error expected by this treatment.

12.3.14 Initial and final masses and actual mass losses for each specimen.

12.3.15 Evaluation of attack if other than general, such as crevice corrosion under support rod, pit depth and distribution, and results of microscopical examination or bend tests.

12.3.16 Corrosion rates for each specimen.

12.4 Minor occurrences or deviations from the proposed test program often can have significant effects and should be reported if known.

12.5 Statistics can be a valuable tool for analyzing the results from test programs designed to generate adequate data. Excellent references for the use of statistics in corrosion studies include Ref. **(5-7)** and in Guide G 16.

13. Keywords

13.1 accelerated; immersion; laboratory; mass loss; metals; pitting

REFERENCES

(**1**) Fisher, A. O., and Whitney, Jr., F. L., "Laboratory Methods for Determining Corrosion Rates Under Heat Flux Conditions," *Corrosion*, Vol 15, No. 5, May 1959, p. 257t.

(**2**) U.S. Patent 3,228,236, 1969.

(**3**) "Stress Corrosion Test Environments and Test Durations," *Symposium on Stress Corrosion Testing*, *ASTM STP 425*, ASTM, 1967.

(**4**) Wachter, A., and Treseder, R. S., "Corrosion Testing Evaluation of Metals for Process Equipment," *Chemical Engineering Progress*, Vol 43, June 1947, pp. 315–326.

(**5**) Mickley, H. S., Sherwood, T. K., and Reed, C. E. editors, *Applied Mathematics in Chemical Engineering* 2nd Edition, McGraw-Hill Book Co., New York, NY 1957.

(**6**) Youden, W. J., *Experimentation and Measurement*, National Science Teachers Assn., Washington, DC, 1962.

(**7**) Booth, F. F., and Tucker, G. E. G., "Statistical Distribution of Endurance in Electrochemical Stress-Corrosion Tests," *Corrosion*, Vol 21, No. 5, May 1965, pp. 173–177.

(**8**) Champion, F. A., *Corrosion Testing Procedures*, 2nd Edition, John Wiley & Sons, Inc., New York, NY, 1965.

Designation: G 59 – 97 (Reapproved 2003)

Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements[1]

This standard is issued under the fixed designation G 59; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes an experimental procedure for polarization resistance measurements which can be used for the calibration of equipment and verification of experimental technique. The test method can provide reproducible corrosion potentials and potentiodynamic polarization resistance measurements.

1.2 *This test method does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing[2]

G 5 Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements[2]

G 102 Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements[2]

2.2 *Adjunct:*

Samples of the Standard AISI Type 430 Stainless Steel (UNS S43000)[3]

3. Significance and Use

3.1 This test method can be utilized to verify the performance of polarization resistance measurement equipment including reference electrodes, electrochemical cells, potentiostats, scan generators, measuring and recording devices. The test method is also useful for training operators in sample preparation and experimental techniques for polarization resistance measurements.

3.2 Polarization resistance can be related to the rate of general corrosion for metals at or near their corrosion potential, E_{corr}. Polarization resistance measurements are an accurate and rapid way to measure the general corrosion rate. Real time corrosion monitoring is a common application. The technique can also be used as a way to rank alloys, inhibitors, and so forth in order of resistance to general corrosion.

3.3 In this test method, a small potential scan, $\Delta E(t)$, defined with respect to the corrosion potential ($\Delta E = E - E_{corr}$), is applied to a metal sample. The resultant currents are recorded. The polarization resistance, R_P, of a corroding electrode is defined from Eq 1 as the slope of a potential versus current density plot at $i = 0$ **(1-4)**:[4]

$$R_p = \left(\frac{\partial \Delta E}{\partial i}\right)_{i=0,\ dE/dt \to 0} \quad (1)$$

The current density is given by i. The corrosion current density, i_{corr}, is related to the polarization resistance by the Stern-Geary coefficient, B. **(3)**,

$$i_{corr} = 10^6 \frac{B}{R_p} \quad (2)$$

The dimension of R_p is ohm-cm ^{2}, i_{corr} is muA/cm^2, and B is in V. The Stern-Geary coefficient is related to the anodic, b_a, and cathodic, b_c, Tafel slopes as per Eq 3.

$$B = \frac{b_a\ b_c}{2.303(b_a + b_c)} \quad (3)$$

The units of the Tafel slopes are V. The corrosion rate, CR, in mm per year can be determined from Eq 4 in which EW is the equivalent weight of the corroding species in grams and ρ is the density of the corroding material in g/cm^3.

$$CR = 3.27 \times 10^{-3} \frac{i_{corr}\, EW}{\rho} \quad (4)$$

Refer to Practice G 102 for derivations of the above equations and methods for estimating Tafel slopes.

3.4 The test method may not be appropriate to measure polarization resistance on all materials or in all environments. See 8.2 for a discussion of method biases arising from solution resistance and electrode capacitance.

4. Apparatus

4.1 The apparatus is described in Test Method G 5. It includes a 1 L round bottom flask modified to permit the

[1] This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals, and is the direct responsibility of Subcommittee G 01.11 on Electrochemical Measurements in Corrosion Testing.

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[2] *Annual Book of ASTM Standards,* Vol 03.02.

[3] Available from ASTM Headquarters. Order PCN 12-700050-00.

[4] The boldface numbers in parentheses refer to the list of references at the end of this standard.

addition of inert gas, thermometer, and electrodes. This standard cell or an equivalent cell can be used. An equivalent cell must be constructed of inert materials and be able to reproduce the standard curve in Test Method G 5.

4.2 A potentiostat capable of varying potential at a constant scan rate and measuring the current is needed.

4.3 A method of recording the varying potential and resulting current is needed.

5. Test of Electrical Equipment

5.1 Before the polarization resistance measurement is made, the instrument system (potentiostat, *X-Y* recorder or data acquisition system) must be tested to ensure proper functioning. For this purpose, connect the potentiostat to a test electrical circuit **(5)**. While more complex dummy cells are sometimes needed in electrochemical studies, the simple resistor shown in Fig. 1 is adequate for the present application.

5.2 Use R = 10.0 Ω. Set the applied potential on the potentiostat to E =– 30.0 mV and apply the potential. The current should be 3.0 mA by Ohm's Law, $I = E/R$.

NOTE 1—When polarization resistance values are measured for systems with different corrosion currents, the value of R should be chosen to cover the current range of the actual polarization resistance measurement. Expected corrosion currents in the microampere range require R = 1 to 10 kΩ.

5.3 Record the potentiodynamic polarization curve at a scan rate of 0.6 V/h from ΔE = –30 mV to ΔE = +30 mV and back to ΔE = –30 mV. The plot should be linear, go through the origin, and have a slope 10 Ω. The curves recorded for the forward and reverse scans should be identical.

5.4 If the observed results are different than expected, the electrochemical equipment may require calibration or servicing in accordance with the manufacturer's guidelines.

6. Experimental Procedure

6.1 The 1.0 N H_2SO_4 test solution should be prepared from American Chemical Society reagent grade acid and distilled water as described in Test Method G 5. The standard test cell requires 900 mL of test solution. The temperature must be maintained at 30°C within 1°.

6.2 The test cell is purged at 150 cm^3/min with an oxygen-free gas such as hydrogen, nitrogen, or argon. The purge is started at least 30 min before specimen immersion. The purge continues throughout the test.

6.3 The working electrode should be prepared as detailed in Test Method G 5. The experiment must commence within 1 h of preparing the electrode. Preparation includes sequential wet polishing with 240 grit and 600 grit SiC paper. Determine the surface area of the specimen to the nearest 0.01 cm^2 and subtract for the area under the gasket (typically 0.20 to 0.25 cm^2).

6.4 Immediately prior to immersion the specimen is degreased with a solvent such as acetone and rinsed with distilled water. The time delay between rinsing and immersion should be minimal.

NOTE 2—Samples of the standard AISI Type 430 stainless steel (UNS S45000) used in this test method are available to those wishing to evaluate their equipment and test procedure from Metal Samples, P.O. Box 8, Mumford, AL 36268.

6.5 Transfer the test specimen to the test cell and position the Luggin probe tip 2 to 3 mm from the test electrode surface. The tip diameter must be no greater than 1 mm.

6.6 Record the corrosion potential E_{corr} after 5 and 55-min immersion.

6.7 Apply a potential 30 mV more negative that the recorded 55 min corrosion potential (See Note 3).

NOTE 3—Practice G 3 provides a definition of sign convention for potential and current.

6.8 One minute after application of the –30 mV potential, begin the anodic potential scan at a sweep rate of 0.6 V/h (within 5 %). Record the potential and current continuously. Terminate the sweep at a potential 30 mV more positive than the 55 min corrosion potential.

6.9 Plot the polarization curve as a linear potential-current density plot as shown in Practice G 3. Determine the polarization resistance, R_p, as the tangent of the curve at i=0.

7. Report

7.1 Report the following information:

7.1.1 The 5 and 55 min corrosion potentials and the polarization resistance value,

7.1.2 Duplicate runs may be averaged, and

7.1.3 Note any deviation from the procedure or test conditions established in this test method.

8. Precision and Bias

8.1 *Precision*—Precision in this test method refers to the closeness of agreement between randomly selected measured values. There are two aspects of precision, repeatability and reproducibility. Repeatability refers to the closeness of agreement between measurements by the same laboratory on identical Type 430 stainless steel specimens repeated with as close as possible adherence to the same procedure. Reproducibility refers to the closeness of agreement between different laboratories using identical Type 430 stainless steel specimens and

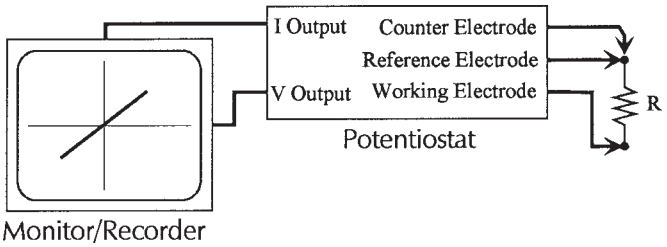

FIG. 1 Arrangement for Testing of Electrical Equipment (Potentiostat, X-Y Recorder)

the procedure specified. An interlaboratory test program with 13 laboratories participating and two, three or four replicate measurements was carried out to establish the precision. The measured values included (Table 1) the corrosion potential measured after 5 and 55 min and the polarization resistance. A research report has been filed with the results of this program.

8.1.1 *Repeatability*— The lack of repeatability is measured by the repeatability standard deviation s_r. The 95 % confidence interval was calculated as ± 2.8 s_r. The values obtained are shown in Table 2.The 95 % confidence interval refers to the interval around the average that 95 % of the values should be found.

TABLE 1 Interlaboratory Test Program Polarization Data for Stainless Steel Type 430 in 1.0 N H_2SO_4 at 30°C

Laboratory	E_{corr}–5min	E_{corr}–55min	R_p
	(mV)	(mV)	(ohm-cm^2)
1	–0.519	–0.506	6.47
	–0.519	–0.505	5.88
2	–0.542	–0.521	5.95
	–0.540	–0.519	5.04
3	–0.524	–0.513	6.93
	–0.520	–0.508	6.40
4	–0.555	–0.545	7.70
	–0.565	–0.545	7.70
5	–0.539	–0.524	7.58
	–0.530	–0.510	6.18
6	–0.519	–0.510	7.60
	–0.522	–0.512	7.16
	–0.521	–0.509	6.65
7	–0.522	–0.510	9.06
	–0.520	–0.511	7.07
	–0.523	–0.510	5.85
8	–0.520	–0.508	7.11
	–0.520	–0.508	7.52
	–0.521	–0.510	6.94
9	–0.529	–0.513	7.11
	–0.530	–0.513	7.22
	–0.529	–0.514	7.19
	–0.529	–0.515	7.19
10	–0.514	–0.505	5.17
	–0.516	–0.506	6.90
11	–0.543	–0.529	5.07
	–0.538	–0.524	4.64
12	–0.520	–0.505	5.63
	–0.519	–0.507	6.16
13	–0.531	–0.519	5.08
	–0.529	–0.517	5.38
	–0.529	–0.517	5.90

TABLE 2 Repeatability Statistics

	Average	S_r	95 % Confidence Interval
E_{corr} 5 min, mV versus SCE	–0.5287	0.00260	± 0.0073 V
E_{corr} 55 min, mV versus SCE	–0.5151	0.00273	± 0.0076 V
R_p, ohm-cm^2	6.46	0.713	±2.00 ohm-cm^2

8.1.2 *Reproducibility*— The lack of reproducibility is measured by the reproducibility standard deviation, s_R. The 95 % confidence interval was calculated as ± 2.8 s_R. The values obtained are shown in Table 3.

TABLE 3 Reproducibility Statistics

	Average	S_R	95 % Confidence Interval
E_{corr} 5 min, mV versus SCE	–0.5287	0.0127	± 0.0356 mV
E_{corr} 55 min, mV versus SCE	–0.5151	0.0111	± 0.0311 mV
R_p ohm-cm^2	6.46	1.01	±2.83 ohm-cm^2

8.2 *Bias*—The polarization resistance as measured by the Test Method G 59 has two sources of bias. The potentiodynamic method includes a double layer capacitance charging effect that may cause the polarization resistance to be underestimated. There is also a solution resistance effect that may cause the polarization resistance to be overestimated. This bias will depend on the placement of the reference electrode and electrolyte conductivity. Refer to Practice G 102 for further discussion on the effects of double layer capacitance and solution resistance on polarization resistance measurements.

9. Keywords

9.1 anodic polarization; auxiliary electrode; cathodic polarization; corrosion; corrosion potential; corrosion rate; current density; electrochemical cell; electrochemical potential; Luggin probe; mixed potential; open-circuit potential; overvoltage; polarization resistance; potentiodynamic; reference electrode; solution resistance; Stern-Geary coefficient; Tafel slope; working electrode

REFERENCES

(**1**) Stern, M., and Roth, R. M., *Journal of the Electrochemical Society*, Vol 104, 1957, p. 390.

(**2**) Stern, M., Corrosion, Vol 14, 1958, p. 440 t.

(**3**) Mansfeld, F., "The Polarization Resistance Technique for Measuring Corrosion Currents", *Corrosion Science and Technology*, Plenum Press, New York, NY, Vol VI, 1976, p.163.

(**4**) Mansfeld, F., "Evaluation of Polarization Resistance Round Robin Testing Conducted by ASTM G01.11", Paper No. 106, CORROSION/76, NACE, Houston, TX, March 22-26, 1976.

(**5**) Gileadi, E., Kirowa-Eisner, E., and Penciner, J. *Interfacial Electrochemistry, an Experimental Approach*, Chapter III.1, Addison-Wesley Publishing Co., Reading, MA 1975.